any basic groups when measured by titration of their acetic acid solutions with perchloric acid dissolved in glacial acetic acid.

Solubility.—All four compounds are very insoluble: in alcohol, acetone, ether, and benzene the solubility is less than 0.1 mg./ml.; chloroform dissolves I and II to a slightly greater extent; pyridine dissolves all to about 1–2%. Neither 6 N hydrochloric acid nor 10% sodium hydroxide dissolves any of them appreciably.

Hydrogenation.—Most experiments were performed with 15–30-mg. portions dissolved in 30 ml. of redistilled glacial acetic acid in an apparatus patterned after that of Ogg and Cooper.[19] As catalysts 150-mg. portions of 10% palladium–carbon or platinum oxide were used, the former for hydrogenation of olefinic bonds only, the latter for hydrogenation of aromatic groups as well. These catalysts were hydrogenated in 10 ml. of glacial acetic acid immediately prior to addition of the solution to be measured and account was taken of the hydrogen consumption by the solvent blank. In the preparation of III from II, only 20 mg. of 10% palladium–carbon was used with 60 mg. of II dissolved in 60 ml. glacial acetic acid; the reaction was stopped when 1 molar equiv. of hydrogen was taken up. For analysis, the product was purified by two extractions with chloroform and by five recrystallizations from acetone.

Hydrolyses. A. Hydrochloric Acid.[20]—The compounds were dissolved in a slight excess of glacial acetic acid and then one-fourth that volume of 25% hydrochloric acid (w./w.) was added; after flushing with nitrogen, the tubes were sealed *in vacuo* and heated at 95° for 48 hr. Generally the hydrolysates were evaporated to dryness, washed with ether (negligible extract except with I and III), and subjected to analysis for ammonia and amino acids on a Spackman–Stein–Moore column.[21] In those cases where a single degradation product was expected, the infrared absorption was also measured. In the total hydrolysate of I a 2 molar proportion of ammonia was measured on the column, and the identity was confirmed by the infrared spectrum which was that of ammonium chloride. Paper chromatography with the total hydrolysate and with its ether extract showed a product moving identically with phenylpyruvic acid: R_f 0.33, n-butyl alcohol saturated with 1.5 N ammonium hydroxide; R_f 0.39, t-butyl alcohol–ammonia (d 0.88)–water (20:1:4); R_f 0.88, butanol–acetic acid–water (12:3:5). Both gave uncommon reactions with these spotting reagents: ferric chloride, a juniper green; 2,6-dichloroindophenol, white on colored background. Also comparison of the infrared spectra of solids from the ether extract and of phenylpyruvic acid confirmed this identification.

B. Sodium Hydroxide.—A suspension of 400 mg. of I in 10 ml. of 1 N sodium hydroxide was heated at 100° for 4 hr. and the volatile products were swept through 2,4-dinitrophenylhydrazine traps which were changed frequently. From the early cuts, the 2,4-dinitrophenylhydrazone of isobutyraldehyde was separated; these yellow crystals melted at 185° with decomposition; an authentic sample melted at 182°, reported m.p. 182° and 187°; the behavior of both hydrazones on paper chromatography was identical: R_f 0.84, 5% ethyl ether in ligroin (b.p. 100–106°), and R_f 0.93, 30% tetrahydrofuran in ligroin. The 2,4-dinitrophenylhydrazone which formed in larger amounts throughout most of the run gave orange crystals, m.p. 243–245° (recrystallized from ethanol); the corresponding derivative of benzaldehyde had m.p. 243° and m.m.p. 242–243°; on paper chromatography both moved at similar rates: R_f 0.51, 5% ether in ligroin, and 0.88, 30% tetrahydrofuran in ligroin. Furthermore, after the mixture of these dinitrophenylhydrazones of the degradation products of I was resolved on a silicic acid–Celite column,[22] infrared absorption and melting point data proved the derivatives to be those of isobutyraldehyde and of benzaldehyde. In similar but smaller scale hydrolyses of I ammonia was identified by a positive Nessler reaction and by recognition of the infrared spectrum of ammonium chloride formed by passing the volatile degradation products through ether saturated with hydrogen chloride.

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[19] C. L. Ogg and F. J. Cooper, *Anal. Chem.*, **21**, 1400 (1949).

[20] C. Kelley and R. Brown, *N. Y. State Dept. of Health Ann. Rept. Div. Lab. Res.*, 75 (1961).

[21] The operation of the Spackman-Stein-Moore column was by Mr. Edward F. Duchna and the data were analyzed by Mrs. Marijane A. McEwan.

[22] B. E. Gordon, F. Wopat, Jr., H. D. Burnham, and L. C. Jones, Jr., *Anal. Chem.*, **23**, 1754 (1951).

Sodium- and Potassium-Catalyzed Reactions of Toluene, Ethylbenzene, and Isopropylbenzene with Isoprene[1,2]

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In the sodium- and potassium-catalyzed alkenylation of alkylarenes with isoprene, the mode of addition seems to be determined by the relative stabilities of the resultant carbanions and also the "size effect" of alkali metal ions in the transition state. The ratios of monoadducts resulting from "head addition" and "tail addition" are 2.77, 1.88, and 1.98 for toluene, ethylbenzene, and isopropylbenzene, respectively, in the presence of sodium; and 3.04, 2.54, and 3.30 for toluene, ethylbenzene, and isopropylbenzene, respectively, in the case of potassium. The relative rates of alkenylation obtained from competitive reactions are as follows: in sodium-catalyzed reactions, 1.00 for toluene, 1.00 for ethylbenzene, and 0.058 for isopropylbenzene; and in potassium-catalyzed reactions, 1.00 for toluene, 1.12 for ethylbenzene, and 0.449 for isopropylbenzene.

The base-catalyzed side-chain alkylation of alkylbenzenes has been the subject of extensive study in our laboratory.[3] This study was recently extended to include the aralkylation of alkylbenzenes with α-methyl- and β-alkylstyrenes.[4,5] The purpose of the present paper is to investigate the addition of alkylbenzenes to the unsymmetrical diolefin isoprene in the presence of sodium and potassium as catalysts in order to gain a better understanding of the mechanism of the side-chain alkylation reaction.

Hoffman and Michael reported a 30% yield of 2-methyl-5-phenyl-2-pentene and 3-methyl-5-phenyl-2-pentene from the reaction of isoprene and toluene at 160° in the presence of sodium.[6] Robertson and Marion observed the presence of side-chain alkenylated products having the general formula $C_6H_5CH_2[CH_2\text{—}C(CH)_3{=}CH\text{—}CH_2]_nH$ (n = 1 to 5) in the sodium-initiated polymerization of isoprene at 90° in toluene solvent.[7] None of the authors gave detailed structures of the products obtained.

In the present study toluene, ethylbenzene, and isopropylbenzene were employed as aromatics, and the structures of the products were determined by means of chemical and physical methods.

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[1] Paper XXVIII of the series "Base-Catalyzed Reactions." For paper XXVII, see J. Shabtai and H. Pines, *J. Org. Chem.*, **29**, 2408 (1964).

[2] This work was supported by the NSF Grant G14503.

[3] For the general review of the literature, see H. Pines and L. Schapp, *Advan. Catalysis*, **12**, 117 (1960).

[4] J. Shabtai and H. Pines, *J. Org. Chem.*, **26**, 4225 (1961).

[5] J. Shabtai, E. M. Lewicki, and H. Pines, *ibid.*, **27**, 2618 (1962).

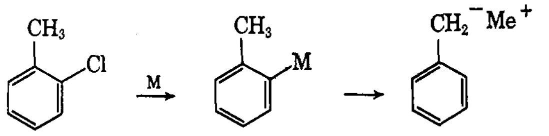
[6] F. Hoffman and A. Michael, U. S. Patent 2,448,641 (1928).

[7] R. E. Robertston and L. Marion, *Can. J. Res.*, **26B**, 657 (1948).

Discussion of Results

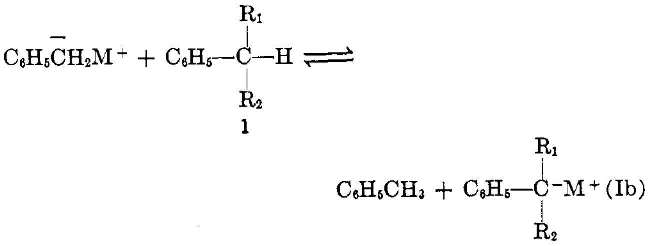
The reactions of the alkylbenzenes with isoprene were carried out at 125 ± 8° in the presence of highly dispersed sodium or potassium as catalyst and *o*-chlorotoluene as a chain initiator. The mechanism of the alkenylation reaction is similar to that of side-chain ethylation of alkylbenzenes[8,9] and can be formulated as follows.

Step I: Initiation[10]



(Ia)

M = Na or K

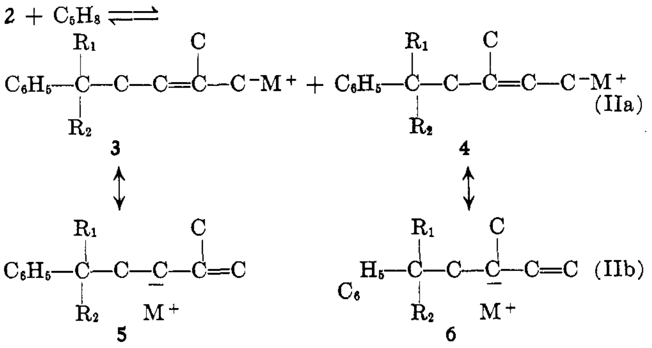


$$C_6H_5\bar{C}H_2M^+ + C_6H_5-\overset{R_1}{\underset{R_2}{C}}-H \rightleftharpoons C_6H_5CH_3 + C_6H_5-\overset{R_1}{\underset{R_2}{C}}{}^-M^+ \quad (Ib)$$

1 2

R_1 and R_2 = H or CH_3

Step II: Pentenylation

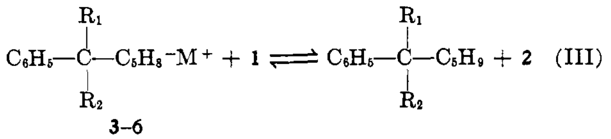


$$\mathbf{2} + C_5H_8 \rightleftharpoons C_6H_5-\overset{R_1}{\underset{R_2}{C}}-C-C=\overset{C}{C}-C^-M^+ + C_6H_5-\overset{R_1}{\underset{R_2}{C}}-C-\overset{C}{C}=C-C^-M^+ \quad (IIa)$$

$$C_6H_5-\overset{R_1}{\underset{R_2}{C}}-C-\underset{M^+}{\bar{C}}-\overset{C}{C}=C \qquad C_6H_5-\overset{R_1}{\underset{R_2}{C}}-C-\overset{C}{\underset{M^+}{\bar{C}}}-C=C \quad (IIb)$$

3 4 5 6

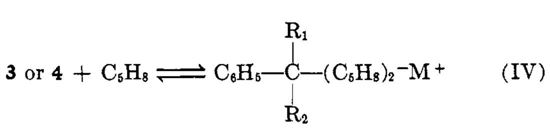
Step III: Proton transfer (or metalation)



$$C_6H_5-\overset{R_1}{\underset{R_2}{C}}-C_5H_8{}^-M^+ + \mathbf{1} \rightleftharpoons C_6H_5-\overset{R_1}{\underset{R_2}{C}}-C_5H_9 + \mathbf{2} \quad (III)$$

3–6

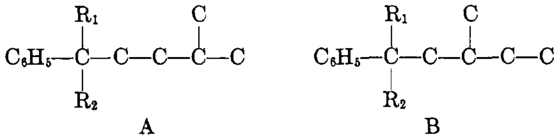
Step IV: Further addition



$$\mathbf{3} \text{ or } \mathbf{4} + C_5H_8 \rightleftharpoons C_6H_5-\overset{R_1}{\underset{R_2}{C}}-(C_5H_8)_2{}^-M^+ \quad (IV)$$

The monopentenylated aromatics formed from toluene and ethylbenzene in step III can also undergo metalation on the benzylic carbon atom to form eventually dipentenylalkylbenzenes of the general formula $C_6H_5C(R_1)(C_5H_9)_2$.

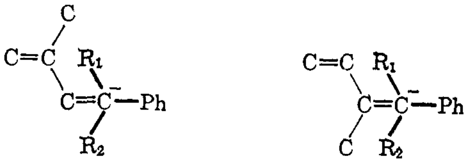
In the present study the main attention will be given to the monoalkenylated aromatics as their structures can be determined and their compositions can be estimated quantitatively. Some of the olefins did undergo a double-bond migration under our experimental conditions. However, the thermodynamically most stable β-alkylstyrenes were not detected (as benzaldehyde after ozonolysis) among the reaction products. The monoadduct fractions were selectively hydrogenated to the corresponding alkylbenzenes in the presence of a 5% palladium on charcoal catalyst. The general structures of the reduced monoadducts can be represented by A and B. The ratios of A to B obtained from the sodium-catalyzed pentenylation of toluene, ethylbenzene, and isopropylbenzene were 2.77, 1.88, and 1.98, respectively. With potassium catalyst the ratio of A to B was 3.04 for toluene, 2.54 for ethylbenzene, and 3.30 for isopropylbenzene (Table II).



$$C_6H_5-\overset{R_1}{\underset{R_2}{C}}-C-C-\overset{C}{C}-C \qquad C_6H_5-\overset{R_1}{\underset{R_2}{C}}-C-\overset{C}{C}-C-C$$

A B

If it is assumed that compounds **3** and **4** have a comparable rate of protonation (step III) and of further addition to isoprene (step IV), then the ratio of the hydrogenated monoadducts A to B reflects the nature of the alkenylation reaction. Type A compounds were the predominant ones, regardless of the catalyst and alkylaromatic used. In order to explain this result, several factors have to be taken into consideration. The nearly planar, partially dissociated, resonance-stabilized, vibrating benzylic carbanion **2** will most likely orient itself parallel to the plane of isoprene in the transition state (T.S.) during alkenylation. In the T.S. the steric effect arising from the methyl group on the isoprene molecule differs little whether the carbanion adds to the head or to the tail of the isoprene molecule (in the structures, light lines represent isoprene molecule, bold lines the carbanion). The preferential formation of type A compounds over type B for the same carbanion is likely to be due to the difference in the stabilities of the resultant carbanions **3** and **4** (1° ⟷ 2° *vs.* 1° ⟷ 3°) and only to a smaller extent to a steric interaction on the addition (step II).



In the sodium-catalyzed reactions, the most stable benzyl carbanion,[11] $C_6H_5CH_2^-$, shows the highest selectivity. This agrees with the generally accepted concept: the less reactive the reactant is, the more selectively it behaves. In the case of ethylbenzene, in the T.S. the methyl group at the benzylic position of 1-

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[8] H. Pines, J. A. Vesely, and V. N. Ipatieff, *J. Am. Chem. Soc.*, **77**, 554 (1955).

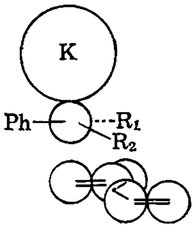
[9] H. Pines and V. Mark, *ibid.*, **78**, 4316 (1956).

[10] H. Gilman and H. A. Pacevitz, *ibid.*, **62**, 673 (1940).

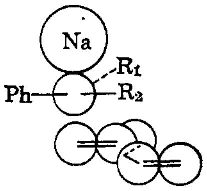
[11] The relative stabilities of 2-phenylalkyl carbanions were described in A. A. Morton, *Chem. Rev.*, **35**, 1 (1944); also see ref. 14.

phenylethide, $C_6H_5C^-HCH_3$, can assume a position which avoids its direct interaction with the methyl group on isoprene. Thus, it does not interfere with its reactivity and gives a lower A to B ratio. Cumyl carbanion, $C_6H_5C^-(CH_3)_2$, would be expected to be the most reactive one; however, it has two methyl groups at its benzylic position, one of which will always oppose the methyl group on isoprene at the T.S. during alkenylation. Therefore, its reactivity is seriously impaired and probably for that reason the A to B ratio was 1.98.

The similar trend of A to B ratios was observed with toluene (3.04), ethylbenzene (2.54), and isopropylbenzene (3.30) from the potassium-catalyzed reactions. However, these reactions gave a greater selectivity for the A-type addition than the respective sodium-catalyzed alkenylations. If the ionic character is an indirect measure of the bond distance between the carbon and the metal, then C–Na and C–K bonds are of the same order (ionic character for C–Na 47%, C–K 52%[12]). The difference in the experimental results obtained with potassium and sodium may be related to their apparent volumes (Na 8.42 Å.[3], K 18.9 Å.[3]) which were estimated from the covalent and ionic volumes of these two metals.[13] The larger size of potassium may tend to force the R_1 and R_2 groups on the benzylic carbon closer to the isoprene molecule causing an unfavorable T.S. during alkenylation (C *vs.* D) and consequently enhancing the selectivity of the reactions. This effect would be most pronounced in the case of cumyl potassium, and gave an A to B ratio of 3.30 as a result.



C



D

The competitive pentenylation data show that the alkenylation of cumene is slower than that of toluene and ethylbenzene. Taking the rate of toluene as unity, the relative rates of ethylbenzene and of isopropylbenzene in the presence of sodium were 1.00 and 0.058, and in the presence of potassium 1.12 and 0.449, respectively. This does not imply that the alkenylation rates of the sodium- and potassium-catalyzed reactions of toluene were the same. With the data available it is difficult to distinguish whether metalation (step III) or alkenylation (step II) is the rate-determining step. If it were metalation, then the relative rates of alkenylation would probably follow the relative acidities of the various alkylaromatics.[14] This was not observed. Similar results were obtained in the competitive ethylation reaction of alkylaromatics.[15]

The diadducts were investigated with the purpose of determining the ratio of the monoadducts **3** and **4** adding to isoprene. For that reason the diadducts obtained from the interaction of toluene with 2 moles of isoprene were ozonized and the products from the cleavage were determined. From the relative amounts of 3-phenylpropanal and 4-phenyl-2-butanone obtained, it was found that the ratio of monoadducts **3** and **4** which added to isoprene was 2.30 for sodium and 2.06 for potassium, respectively (Table IV). This ratio is somewhat smaller than the ratio of compounds of type A and B found. The difference may be due to the fact that some of the 3-phenylpropanal was converted to its corresponding acid which would not elute out under our v.p.c. analysis conditions.

This type of lengthening of the alkyl chain by multiple addition to isoprene (step IV) was not encountered in the case of ethylation of alkylaromatics in which the di- and triadducts were formed on the benzylic carbon only.[3] Evidently the intermediate carbanions, **3** and **4**, owing to their resonance stabilization and therefore longer life, are able to add to another molecule of isoprene at rates comparable with their protonation.

Experimental

All melting points are uncorrected and were taken on a Fisher-Johns heating block.

The infrared spectra of pure liquid samples were taken in a 0.026-mm. sodium chloride cell against a sodium chloride prism with either a Baird Model AB-2 or 4–55 calibrated at 6.24 and 11.03 μ with polystyrene film.

Vapor phase chromatographic analyses and separations (manual) were performed with a F and M Model 300 or 720, over the column(s) listed in Table I.

TABLE I

DESCRIPTION OF VAPOR PHASE CHROMATOGRAPHIC COLUMNS

Column	Liquid phase	Solid support	Mesh	Length, m.	o.d., in.
A	33% Dimethylsulfolane	Firebrick	100–120	4.56	0.25
B	15% Carbowax 20 M	Chromosorb P	35–60	2.0	0.25
C	10% Silicone oil DC-550	Chromosorb P	30–60	4.0	0.25
D	25% QF-1	Chromosorb P	80–100	8.0	0.25
E	24% Squalane	Chromosorb P	80–100	3.1	0.25
F	12% Silicone oil DC-550	Chromosorb P	30–60	5.0	0.375

Reagents.—Toluene (Matheson CB810), ethylbenzene (Matheson 5026), and isopropylbenzene (Matheson 2849) were refluxed over sodium, and then distilled through a spinning-band column; the fractions collected had b.p. 110.5–111.0°, 135.5–136.0°, and 152.0–152.2°, respectively. Isoprene (Eastman 2542) was dried over sodium and distilled just before use, b.p. 34.5–35.0°. Their purities were >99.5% adjudged by v.p.c.

General Procedure and Apparatus for Alkenylation Reaction.—A high-surface catalyst was prepared separately in a three-necked round-bottom flask, equipped with a specially designed drum-shaped high-speed stirrer, and a condenser to which a potassium hydroxide drying tube was attached. Under nitrogen atmosphere, freshly cut alkali metal (0.050 g.-atom) was dispersed in a solution of arylalkane (1.0 mole) and *o*-chlorotoluene (0.0043 mole) at reflux temperature for 2–2.5 hr. An active catalyst should be in the form of a powder with brownish black coloration. The mixture was then cooled and transferred to a Magne-Dash Autoclave (Autoclave Engineers, Inc.) of 250-ml. capacity. After replacing the air in the autoclave by flushing repeatedly with nitrogen, the mixture was heated up to the reaction temperature (about 125°) while under constant agitation. Isoprene (0.50

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[12] E. G. Rochow, D. T. Hurd, and R. N. Lewis, "The Chemistry of Organometallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 65.

[13] T. Moeller, "Inorganic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 135, p. 139.

[14] (a) A. I. Shatenshtein and E. A. Izrealvich, *Zh. Fiz. Khim.*, **32**, 2711 (1958); (b) A. Streitwieser, Jr., and D. E. Van Sickle, *J. Am. Chem. Soc.*, **84**, 249 (1962); (c) J. E. Hofmann, R. J. Muller, and A. Schriesheim, *ibid.*, **85**, 3002 (1963).

[15] H. Pines and L. Schaap, *ibid.*, **80**, 3076 (1958).

TABLE II

REACTION CONDITIONS AND PERTINENT DATA OF ALKENYLATION REACTION

Experiment[a],[b]	Catalyst	RPh used, R	Monoadducts: % yield[c]	B.p., °C. (mm.)	$n^{°C.}_D$	Hydrogen no.[d]	Ratio A/B
1	Na	Me	32.2	48(1.7)-59(2.5)	1.5041^{31}	1.01	2.77
2	Na	Et	31.4	101-108(16)	1.5053^{25}	1.08	1.88
3	Na	*i*-Pr	17.4	122(21)-129(19)	1.5047^{25}	1.16	1.98
4	K	Me	38.2	60-66.5(3.3)	1.5038^{31}	1.01	3.04
5	K	Et	58.0	100-105(14)	1.5078^{19}	0.948	2.54
6	K	*i*-Pr	15.7	135-138(30)	1.5044^{25}	1.06	3.30

[a] Temperature: 125 ± 8°. [b] A trace of gases was formed during the reaction (less than 1%). It consisted of 2-methylpentane, 2-methyl-2-pentenes, 2-methyl-1-pentene, and 3-methyl-1-pentene. [c] Based on the isoprene used. [d] Moles of hydrogen absorbed/mole of hydrocarbons used.

mole) was then introduced into the autoclave during a period of 1 hr. by means of a calibrated pressure charger and the mixture was kept at that temperature for another hour. At the end of this period, the isoprene was totally reacted. The gaseous products were released from the autoclave, collected in a gas bottle over a saturated brine solution, and the autoclave was allowed to cool. The remaining catalyst was decomposed with ethanol (for sodium) or isobutyl alcohol (for potassium). The reaction mixture was washed with salt solution, and then with water until neutral. The organic layer was dried over anhydrous magnesium sulfate and finally distilled under nitrogen atmosphere. The composition of the distillates was determined by v.p.c.

Competitive alkenylation experiments were performed under conditions similar to those stated above, except that 1 mole of an equimolar mixture of arylalkanes (0.33 mole of each of toluene, ethylbenzene, and isopropylbenzene) was used; and 0.050 mole of isoprene was added (total reaction time was 20 min.). The reaction mixtures were analyzed after decomposition without further treatment.

Reaction conditions and pertinent data are given in Table II.

Identification of Reaction Products from Alkenylation Reactions.—Gaseous products were analyzed and identified over column A by v.p.c.

Olefinic monoadducts were first hydrogenated (with 5% Pd-C) and the corresponding arylalkanes were identified. Their infrared spectra and relative retention times in v.p.c. analyses (Table III) agreed with the synthetic samples.

Further confirmation of these olefinic monoadducts came from ozonolysis data.

TABLE III

RELATIVE RETENTION TIMES OF HYDROGENATED MONOADDUCTS AND SYNTHETIC ARYLALKANES

	Column B	Column C	Column D	Column E
Temp., °C.	125	125	100	125
Flow rate, cc./min.	80-85	60-65	80-85	120-125
1-Phenylpentane (standard)	1.00	1.00	1.00	1.00
1-Phenyl-4-methylpentane (**7, 23**)		1.38		
1-Phenyl-3-methylpentane (**8, 24**)		1.46		
2-Phenyl-5-methylhexane (**9, 25**)		1.64	1.52	1.78
2-Phenyl-4-methylhexane (**10, 26**)		1.64	1.43[a] 1.57	1.65[a] 1.77
2,5-Dimethyl-2-phenylhexane (**11, 27**)	1.88	2.36		2.59
2,4-Dimethyl-2-phenylhexane (**12, 28**)	1.96	2.36		2.72

[a] There are two asymmetric carbons in compounds **10** and **26**. Each pair of *dl*-racemate exhibits one peak in v.p.c. analysis.

Ozonolysis of the Olefinic Alkenylation Products.—Ozonolysis was carried out at −70° in anhydrous ethyl acetate (sample-solvent, 1:15 by volume) containing phenylcyclohexane, an inert hydrocarbon, as internal v.p.c. standard. Once the ozonolysis was over, the resultant solution was purged with air, and the ozonides were hydrogenated immediately with 5% Pd-C. Anhydrous conditions and sufficient purging were necessary in order to minimize the formation of undesired acid(s) instead of the expected aldehyde(s). The products, corresponding ketone(s) and aldehyde(s), were analyzed by v.p.c. over column B, and their amounts were calculated (Table IV).

TABLE IV

COMPOSITION OF OZONOLYSIS PRODUCTS

Starting olefins	R_1	R_2	Ratio of products[a] E:F:G	% yield
Monoadducts from experiment				
1	H	H	3.02:0.51:1.00	79.2
4	H	H	2.86:0.39:1.00	90.0
2	CH_3	H	1.82:0.25:1.00	66.5
3	CH_3	CH_3	2.69:0.063:1.00	57.3
Diadducts from experiment				
1	H	H	2.30:0.0:1.00	9.7
4	H	H	2.06:0.0:1.00	20.2

[a] E, Ph-C(R_1)(R_2)-C-CHO; F, Ph-C(R_1)(R_2)-C-C-CO-C; G, Ph-C(R_1)(R_2)-C-CO-C. The conversion factors (molar area/mole) used were 0.80 for aldehydes, 1.00 for phenylcyclohexane (standard), and 1.07 for ketones in v.p.c. analyses over column B.

Synthesis of 4-Methyl-4-phenyl-2-pentanone (13).—Mesityl oxide (150 g., 1.6 moles) was treated with benzene in the presence of aluminum chloride, according to the procedure described previously.[9] The yield of compound **13** (239 g., 1.36 moles) was 85%: b.p. 120-132° (15 mm.), $n^{20}D$ 1.5112; lit.[9] b.p. 91.8-95.5° (3.5 mm.), $n^{20}D$ 1.5107.

Synthesis of 3-Methyl-3-phenylbutyric Acid (14).—Compound **14** was prepared from 141 g. (0.80 mole) of compound **13**, 264 g. (6.6 moles) of sodium hydroxide in 2240 ml. of water, and 123 ml. (2.4 moles) of bromine, after the method of Sandborn and Bousquet.[16] The acid **14** boiled at 165° (16 mm.): m.p. 57-58°; lit.[17] b.p. 156.5-160° (10 mm.), m.p. 58-59°. The yield was 84% (119 g., 0.68 mole).

Synthesis of 3-Methyl-3-phenyl-1-butanol (15).—Compound **14** (21.5 g., 0.12 mole) was reduced by an ethereal solution of lithium aluminum hydride (5.7 g., 0.15 mole) in the similar manner described by Pines and Schaap.[17] The alcohol **15** produced amounted to 17.2 g. (0.11 mole, 87%): b.p. 137-142° (16 mm.), $n^{25}D$ 1.5234; lit.[17] b.p. 127-127.5 (10 mm.), $n^{20}D$ 1.5227.

Synthesis of 1-Bromo-3-methyl-3-phenylbutane (16).—Noller and Dinsmore's procedure[18] was used in preparing compound **16**. Starting with 82 g. (0.50 mole) of compound **15** and 15.8 ml., (0.167 mole) of phosphorus tribromide, 72 g. (0.32 mole, 64%) of bromide was obtained, b.p. 101-107° (6 mm.), $n^{21}D$ 1.5400.

Syntheses of Intermediate Carbinols (Table V).—Intermediate carbinols (**17-22**) were synthesized according to the standard Grignard procedure. An ammonium chloride solution was used for acidification during the work-up in order to avoid dehydration of the resultant tertiary carbinol. The crude products were

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TABLE V

SYNTHESES OF INTERMEDIATE CARBINOLS

Carbinol	Reactants: Bromide	Reactants: Carbonyl	Yield, %	B.p., °C. (mm.)	$n^{\circ\mathrm{C.}}_{\mathrm{D}}$
2-Methyl-5-phenyl-2-pentanol (**17**)	γ-Bromopropylbenzene	Acetone	91[a]	...	1.5092^{23b}
1-Phenyl-3-methyl-3-pentanol (**18**)	β-Bromoethylbenzene	2-Butanone	86[a]	...	1.5098^{21b}
2-Phenyl-5-methyl-2-hexanol (**19**)	Isopentyl bromide	Acetophenone	29	138–141 (23)	1.5047^{23}
2-Phenyl-4-methyl-3-hexanol (**20**)	2-Bromobutane	2-Phenylpropanal	40	118–121 (24)	1.5242^{23}
2,5-Dimethyl-5-phenyl-2-hexanol (**21**)	1-Bromo-3-methyl-3-phenylbutane (**16**)	Acetone	56	110.5 (4.8)	1.5089^{22}
2,5-Dimethyl-5-phenyl-3-hexanol (**22**)	Ethyl bromide	4-Methyl-4-phenyl-2-pentanone (**13**)	62	141–144 (19)	1.5128^{22}

[a] Based on crude product (>90% purity). [b] Crude product was measured.

TABLE VI

PHYSICAL CONSTANTS OF SYNTHETIC ARYLALKANES[a]

Compd.	$n^{\circ\mathrm{C}}_{\mathrm{D}}$ Lit.	$n^{\circ\mathrm{C}}_{\mathrm{D}}$ Found	B.p., °C. (mm.) Lit.	B.p., °C. (mm.) Found	Infrared λ, μ $-\mathrm{C}{<}^{\mathrm{C}^{j}}_{\mathrm{C}}$	Infrared λ, μ Benzylic subst.[k]	Formula	C, % Calcd.	C, % Found	H, % Calcd.	H, % Found
26	...	$1.4845^{23.5}$	214–215[g]	*i*	8.50	13.37	$C_{12}H_{18}$	88.82	89.10	11.18	10.95
27	1.4859^{25b} $1.4896^{14.5c}$	$1.4861^{23.5}$	112 (15)[h] 90–91 (9)[c]	*i*	..	13.42	$C_{12}H_{18}$	88.82	88.56	11.18	11.28
28	1.4886^{20d}	1.4834^{24}	65.5–66 (1.5)[d]	111–112 (24)	8.50	13.11	$C_{13}H_{20}$	88.58	88.85	11.44	11.28
29	...	1.4861^{24}	...	103–106 (13)	..	13.13	$C_{13}H_{20}$	88.58	88.71	11.44	11.39
30	1.4885^{20e}	1.4883^{24}	78 (3)[e]	*i*	8.48	13.05	$C_{14}H_{22}$	88.35	88.26	11.65	11.74
31	1.4920^{20f}	1.4921^{24}	112–115 (17)[f]	*i*	..	13.03	$C_{14}H_{22}$	88.35	88.57	11.65	11.58

[a] For relative retention times, see Table III. [b] Levorotatory form, ref. 19. [c] Dextrorotatory form, ref. 20. [d] Ref. 21. [e] Ref. 22. [f] Ref. 23. [g] Ref. 24. [h] Ref. 25. [i] Purified by v.p.c. over column F at 175°. [j] Ref. 26. [k] Ref. 27.

analyzed by v.p.c. (column B) and infrared spectroscopy. Those (**17** and **18**) having purities better than 90% were used directly in the next step of synthesis without further purification. Purification of carbinols **20** and **22** was achieved by chromatography on an aluminum oxide column (aluminum oxide–sample, 25 ml.: 1 ml.), using *n*-pentane as solvent. Desired carbinols would remain on the column until eluted with propanol.

Synthesis of 1-Phenyl-4-methylpentane (23), 1-Phenyl-3-methylpentane (24), 2-Phenyl-5-methylhexane (25), 2-Phenyl-4-methylhexane (26), 2,5-Dimethyl-2-phenylhexane (27), and 2,4-Dimethyl-2-phenylhexane (28) (Table VI).—Dehydration of alcohols **17**, **18**, and **19** was achieved by a catalytic amount of powdered potassium bisulfate at the reflux temperature of toluene which served as a water carrier. Subsequent catalytic hydrogenation with 5% Pd–C gave correspondingly 1-phenyl-4-methylpentane (**23**), 1-phenyl-3-methylpentane (**24**), and 2-phenyl-5-methylhexane (**25**).

A mixture of 5.4 g. (0.028 mole) of alcohol **20**, 3.85 g. (0.032 mole) of phenyl isocyanate, and 0.5 ml. (0.0062 mole) of dried pyridine, excluded from moisture, was kept on a steam bath for 2.5 hr. The urethan of compound **20** crystallized out slowly on standing, and was purified by dissolving it in hot *n*-heptane, then immediately filtering off the insoluble material, *i.e.*, N,N′-diphenylurea, from the hot solution. Recrystallized urethan weighed 4.2 g. (0.0135 mole, 48%). After further purification by sublimation at 100° (5 mm.), the urethan had m.p. of 92–94°. The pyrolysis of the urethan was achieved by heating it in a sealed tube at about 300° for 6 hr. The resultant olefins (64%) were separated from aniline by means of an alumina column (alumina–sample, 10 ml.: 1 ml.). Catalytic hydrogenation with 5% Pd–C gave 2-phenyl-4-methylhexane (**26**).

Alcohols **21** and **22** were dehydrated over Harshaw alumina catalyst at skin temperature of 335°. 2,5-Dimethyl-2-phenylhexane (**27**) and 2,4-dimethyl-2-phenylhexane (**28**) were obtained correspondingly after catalytic hydrogenation over 5% Pd–C

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