scribed in r, produced 18.5 g. (81.1%) of 3,4-dichloro-2-aminonaphthalene-6,8-disulfonic acid, a gray crystalline powder.

Acknowledgment.—The author is indebted to Mr. D. W. Heinritz for spectral measurements and interpretations, to Mr. A. J. Valerga and Mrs. Jane Clark for analytical determinations, to Messrs. E. Nylund and M. L. Deinzer for technical assistance and to Mr. J. K. Frye for assistance in the preparation of the manuscript. The discussions and encouragement provided by Dr. Julius Hyman are gratefully acknowledged.

Potassium-Catalyzed Reactions of β-Alkylstyrenes and Anethol with Alkylbenzenes[1]

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β-Methyl-, β-ethyl-, and β-isopropylstyrene react with toluene at 110° in the presence of dispersed potassium to form the corresponding 1,3-diphenyl-2-alkylpropanes in 60–95% yields. Anethol reacts similarly to form 1-p-methoxyphenyl-2-methyl-3-phenylpropane in 68% yield. β,β-Dimethylstyrene, however, fails to react with toluene. β-Ethylstyrene undergoes also ring closure with the formation of 1-methylindene.

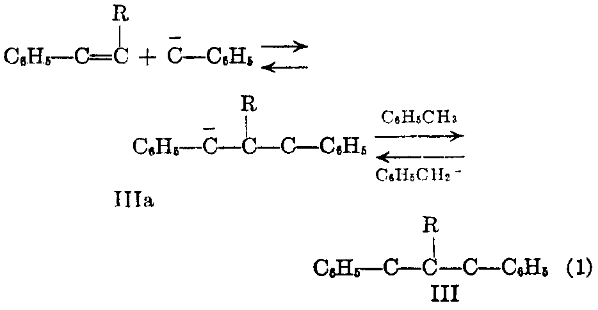
It was reported recently that α-methylstyrene[4] reacts with n-alkylbenzenes in the presence of dispersed potassium to form 1,3-diphenylalkanes in high yield and purity. The study indicated that the introduction of a methyl substituent in the vinyl group of the styrene molecule, unlike ring substitution,[5] increases sharply the selectivity of the aralkylation reaction. As an extension of this study we are reporting the reactions of alkylbenzenes with a series of β-alkylstyrenes in the presence of potassium as catalyst. The influence of the type and number of β-substituents upon the relative rate of aralkylation was examined by a comparative study of the addition reactions of toluene to β-methyl-, β-ethyl-, β-isopropyl-, and β,β-dimethylstyrene. The reactions were carried out in the presence of an excess of toluene. The study of the reaction with anethol was undertaken with the purpose of obtaining information on the possible application of the synthesis to alkoxy derivatives.

A comparative study of the aralkylation of β-methylstyrene with toluene, ethyl-, propyl-, and isopropylbenzene was also carried out in order to determine the effect of the substituent in the alkylbenzene reactant upon the addition reaction.

The experimental procedure was similar to that described previously.[4,5] The reaction products were separated and analyzed by a combination of fractional distillation, selective hydrogenation, ozonization, gas chromatography, infrared and ultraviolet spectroscopy.[1,4,5] The 1,3-diphenylalkanes formed in the reactions were also compared with synthetically prepared samples. The results are summarized in Tables I and II.

Discussion

β-Methyl-, β-ethyl-, and β-isopropylstyrene react with toluene to form the corresponding 1,3-diphenyl-2-alkylpropanes (III) in yields of 60 to 95% (Table I):



$$C_6H_5-C=\overset{R}{\overset{|}{C}} + \bar{C}-C_6H_5 \rightleftarrows \underset{\text{IIIa}}{C_6H_5-C-\overset{R}{\overset{|}{\bar{C}}}-C-C_6H_5} \xrightleftharpoons[C_6H_5CH_2^-]{C_6H_5CH_3} \underset{\text{III}}{C_6H_5-C-\overset{R}{\overset{|}{C}}-C-C_6H_5} \quad (1)$$

The reaction with β-isopropylstyrene, however, is relatively slow, probably as a result of steric hinderance due to the isopropyl group. The steric effect of a β-substituent may be due either to interference with the approach of the benzyl carbanion to the β-position in the addition step of the above reaction and/or to a hindering action preventing the protonation of the adduct carbanion IIIa. The steric effect is sharply increased by introducing a second substituent in the β-position. β,β-Dimethylstyrene, for instance, fails to react with toluene (experiment 6), but instead undergoes

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(1) Paper XXIII of the series *Base-catalyzed Reactions*. For paper XXII, see H. Pines and J. Shabtai, *J. Am. Chem. Soc.*, **83**, 2781 (1961).

(2) National Science Foundation Postdoctoral Fellow, 1960–1961.

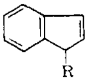
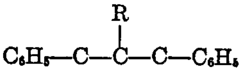
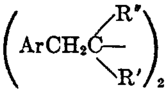
(3) On leave of absence from the Weizmann Institute of Science, Rehovoth, Israel.

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

(5) H. Pines and J. Shabtai, *J. Org. Chem.*, **26**, 4220 (1961).

TABLE I

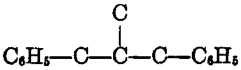
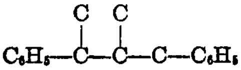
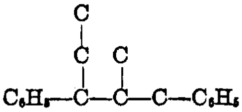
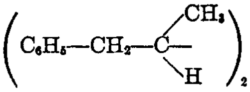
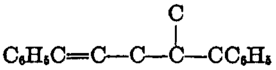
COMPOSITION OF PRODUCTS OBTAINED FROM THE POTASSIUM-CATALYZED REACTIONS OF β-ALKYLSTYRENES AND OF ANETHOL WITH TOLUENE

Experiment	1	2	3	4	5	6
ArC = CR used[a]						
R =	CH_3	CH_3	C_2H_5	i-C_3H_7	i-C_3H_7	$(CH_3)_2$
Ar =	C_6H_5	p-$CH_3OC_6H_4$	C_6H_5	C_6H_5	C_6H_5	C_6H_5
Reaction time, hr.	2	2	2	2	5	2
Conversion,[b] mole %	67.7	32.0	64.4	19.5	43.2	20.0
Product component, wt. %						
ArC—CR (I)	3.5	2.0	9.8	<1.0	<1.0	—
 (II)	—	—	11.6	2.0	2.5	—
 $C_6H_5—C—\overset{R}{C}—C—C_6H_5$ (III)	58.7	68.0[c]	69.2	96.0	95.0	—
 (IV)	15.8[d]	[10.8][d,e]	5.6[f,e]	—	—	~100
Open-chain dimers (V)	18.9[h]	7.0	1.8	—	—	—
Polymeric residue	3.1	12.2	2.0	<1.0	<1.0	—

[a] In each experiment were used 0.1 mole of the β-alkylstyrene (or anethol), 1.0 mole of toluene and 1 g. of potassium; reaction temp., 109–110°. [b] Calcd. on β-alkylstyrene or anethol used. [c] 1-p-Methoxyphenyl-2-methyl-3-phenylpropane. [d] R′ = H, R″ = CH_3. [e] Tentative structure. Compound is under separate investigation. [f] R′ = H, R″ = C_2H_5. [g] R′ and R″ = CH_3. [h] Composed of 2-benzyl-3-phenylpentane, 28.4% and 1,5-diphenyl-4-methyl-1-pentene, 71.6%.

TABLE II

COMPOSITION OF PRODUCTS OBTAINED FROM THE POTASSIUM-CATALYZED REACTIONS OF β-METHYLSTYRENE WITH ALKYLBENZENES

Experiment	7	8	9	10	11
C_6H_5R used[a]					
R =	CH_3	CH_3	C_2H_5	n-C_3H_7	i-C_3H_7
Reaction time, hr.	2	4	2	2	2
Conversion,[b] mole %	58.2	76.0	50.5	64.3	52.6
Product component, wt. %					
	4.8	2.6	2.7	[c]	0.2
 $C_6H_5—C—\overset{C}{C}—C—C_6H_5$ (VII)	47.8	52.3	3.8	1.0	4.1
 $C_6H_5—\overset{C}{C}—\overset{C}{C}—C—C_6H_5$ (VIII)	—	—	33.0	—	—
 $C_6H_5—\overset{C}{\overset{C}{C}}—\overset{C}{C}—C—C_6H_5$ (IX)	2.5	4.4	4.8	19.3	6.0
 (X)	23.1	25.8	31.0	24.8	49.2
 $C_6H_5C{=}C—C—\overset{C}{C}—CC_6H_5$ (XI)	20.3	5.6	22.1	50.6	38.2
High boiling residue	1.5	9.3	2.6	4.3	2.3

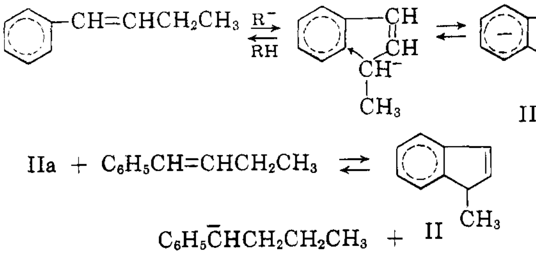
[a] In each experiment were used 0.1 mole of β-methylstyrene, 0.65 mole of alkylbenzene and 1 g. of potassium; 0.2 ml. of a promoter (o-chlorotoluene) was added in experiments 10 and 11. Reaction temperature, 105 ± 2°. [b] Calcd. on β-methylstyrene used. [c] No attempt was made to determine the amount of this hydrocarbon formed during the reaction because of its use as a reagent.

hydrodimerization to form 1,4-diphenyl-2,2,3,3-tetramethylbutane.[6]

The addition of toluene to anethol, resulting in the formation of 1-*p*-methoxyphenyl-2-methyl-3-phenylpropane in 68% yield (experiment 2), indicates that methoxy groups, present as substituents in the benzene ring of the styrene molecule, remain unaffected under the experimental conditions used.

The extent of the competing dimerization reactions[1] of the examined β-alkylstyrenes, leading to the formation of IV and V (Table I), decreases sharply on passing from β-methyl- to β-ethylstyrene and becomes nil in the case of β-isopropyl styrene.

1-Methylindene was detected in the product in the reaction with β-ethylstyrene (experiment 3). The compound is probably derived from the latter by intramolecular alkylation, followed by hydride transfer:



(2)

The simultaneous formation of a nearly equimolal amount of *n*-butylbenzene is in support of the above proposed mechanism. Reaction 2 takes place also when toluene is replaced by a neutral solvent—*e.g.* methylcyclohexane. No detectable amounts of indene were observed in the product of the reaction with β-methylstyrene.

Comparison of the results in Table II with those obtained in the corresponding aralkylation reactions of α-methylstyrene,[4] under identical experimental conditions, points to a considerably more pronounced steric effect of a β-methyl as compared to an α-methyl substituent in the styrene molecule.

At 105° the reaction of normal alkylbenzenes with α-methylstyrene[4] is completed in less than two hours. The yield of the monoadducts is high (75–85%) and apparently independent on the length of the alkyl substituent. Cumene reacts to the extent of about 10% with α-methylstyrene.

In the case of β-methylstyrene (Table II) the reaction with toluene is not completed even after four hours (experiment 8). A comparison of the concentration of compounds VII, VIII, and IX in experiments 7, 9, and 10, respectively, indicates that the relative rate of addition of normal alkylbenzenes to β-methylstyrene decreases sharply with increased length of the alkyl substituent. Furthermore, cumene fails to react with β-methylstyrene (experiment 11). The extent of aralkylation with *n*-alkylbenzenes can be increased by using a higher ratio of alkylbenzene to β-methylstyrene (compare, for instance, experiment 1 with experiment 7).

The importance of the competing dimerization reactions of β-methylstyrene,[1] leading to compounds X and XI, increases sharply with the length and branching of the alkylbenzene reactant (Table II).

Experimental

Apparatus and procedure. The apparatus and experimental procedure were essentially the same used in previous work.[1,4,5]

Identification of reaction products. The analytical methods were similar to those applied before.[1,4,5] Products were

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[6] NOTE ADDED IN PROOF. Professor S. Winstein and Dr. S. J. Lapporte called to our attention that the compound of dimerization of β,β-dimethylstyrene which we reported as having the formula of 1,1,3,3-tetramethyl-2,4-diphenylcyclobutane (I) had the same melting point as 1,4-diphenyl-2,2,3,3-tetramethylbutane (II) which they had prepared as an authentic specimen of rearranged dimer from the neophyl radical.

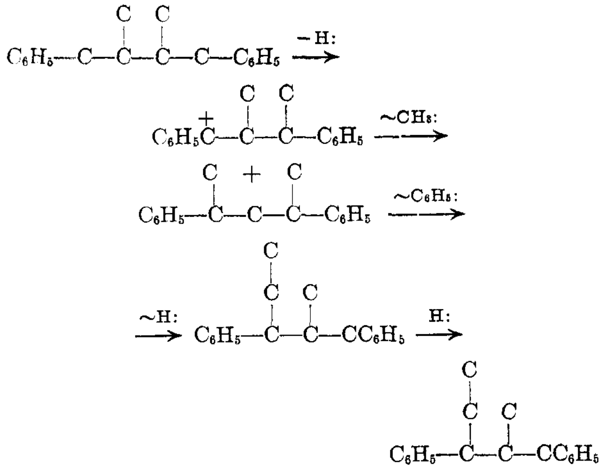
It was indeed found by mixed melting point and by comparison of NMR spectra that the two compounds were identical. The mass spectra determined by Winstein and Lapporte and further study of the NMR by us showed the structure of this solid "dimer" to be II.

In view of the above the structure of the dimer of β-methylstyrene was also reinvestigated.

Originally we assigned the structure of stereoisomers of 1,3-dimethyl-2,4-diphenylcyclobutane to this compound[1] and the assignment of the structure was based primarily on the results of the hydrogenolysis reaction which formed 1,3-diphenyl-2-methylpentane.

This dimer was compared with a "dimer" of β-methylstyrene prepared by a similar method by Winstein and Lapporte and to which they assigned the structure of *erythro*- and *threo*-1,4-diphenyl-2,3-dimethylbutane. Professor Winstein's and our "dimeric" compounds had exactly the same retention times on vapor phase gas chromatography. We synthesized the mixture of *erythro*- and *threo*-1,4-diphenyl-2,3-dimethylbutane by independent means and found it to be the same as the compound we erroneously reported as having the cyclobutane skeletons.

On re-examining the catalyst which we used for hydrogenolysis, we found that it contained some acidic sites which caused skeletal isomerization reactions, which could be explained as follows:



We are indebted to Professor Winstein for bringing this matter to our attention.

TABLE III

Synthesis of Intermediate Carbinols or Keto Olefins

Reactants			Yield,		
Halide	Ketone	Product	%	B.P./Mm.	n_D^{20}
Benzyl chloride	Phenyl-2-propanone	1,3-Diphenyl-2-methyl-2-propanol[a]	74	192/14	1.5700
(1-Bromoethyl)benzene	Phenyl-2-propanone	1,3-Diphenyl-2-methyl-2-butanol[a]	30	159–160/1	1.5698
Bromoethane	1,3-Diphenyl-2-propanone	1,3-Diphenyl-2-ethyl-2-propanol[a]	23	151–152/1	1.5640
2-Bromopropane	1,3-Diphenyl-2-propanone	1,3-Diphenyl-2-isopropyl-2-propanol[a]	18	164–165/1	1.5732
—	Propiophenone[b]	2-Benzoyl-3-phenyl-2-pentene[c]	42	132–133/0.3	1.5882

[a] Elemental analysis agrees within ±0.3% with the calculated values. [b] Claisen-Shmidt condensation (see text). [c] Calcd. for $C_{18}H_{18}O$: C, 86.35; H, 7.25. Found: C, 86.28; H, 7.32.

TABLE IV

Synthesis and Physical Properties of 1,3-Diphenylalkanes

Diphenylalkane	Yield, %[a]	B.P.	Mm.	n_D^{20}	$Rv/Rv_{n\text{-hexyl}}$ Benzene[b]	C, %	H, %
1,3-Diphenyl-2-methylpropane[c]	84	105–106	0.4	1.5520	5.4	91.28[d]	8.60[d]
1,3-Diphenyl-2-methylbutane	80	110–111	0.4	1.5494	6.7	91.05[e]	8.90[e]
1,3-Diphenyl-2-ethylpropane	85	113	0.4	1.5490	6.8	90.88[e]	9.06[e]
1,3-Diphenyl-2-isopropylpropane	78	119–120	0.4	1.5442	8.3	90.52[f]	9.42[f]
1,3-Diphenyl-2-methylpentane	91	115–116	0.4	1.5374	8.0	90.55[f]	9.30[f]

[a] Based on intermediate carbinol or keto olefin. [b] Temp. 225°; 12-ft. column, packed with 8% silicon (Dow-Corning 550 fluid) on 60–80 mesh celite; helium flow rate 125 ml./min. [c] R. M. Caves *et al.*, *J. Am. Chem. Soc.*, **76**, 552 (1954); b.p. 303° at 760 mm., n_D^{29} 1.5519. [d] Calcd. for $C_{16}H_{18}$: C, 91.37; H, 8.63. [e] Calcd. for $C_{17}H_{20}$: C, 91.01; H, 8.99. [f] Calcd. for $C_{18}H_{22}$: C, 90.67; H, 9.31.

identified in most of the cases by comparison of their infrared spectra and retention volumes with those of pure synthetic hydrocarbons.

1-p-Methoxyphenyl-2-methyl-3-phenylpropane, obtained in expt. 2 (Table I), was isolated in nearly 99% purity. Its identity was confirmed by alternative synthesis involving the aralkylation of β-methylstyrene with *p*-methylanisole. The compound had b.p. 131–132° at 0.3 mm., n_D^{20} 1.5560.

Anal. Calcd. for $C_{17}H_{20}O$: C, 84.94; H, 8.40. Found: C, 84.98; H, 8.56.

Synthesis of hydrocarbons. The preparation and properties of the β-alkylstyrenes will be reported elsewhere.

1,3-Diphenyl-2-methylpropane and 1,3-diphenyl-2-methylbutane were prepared through the Grignard reaction of phenyl-2-propanone with benzylchloride and 1-bromoethylbenzene, respectively. The resulting carbinols were dehydrated at 320–340° over Harshaw alumina[7] and the olefins[8] thus obtained were selectively hydrogenated in the presence of a copper chromite catalyst.

1,3-Diphenyl-2-ethylpropane and 1,3-diphenyl-2-isopropylpropane were synthesized in a similar way through the Grignard reaction of 1,3-diphenyl-2-propanone with bromoethane and 2-bromopropane, respectively.

1,3-Diphenyl-2-methylpentane was prepared by the Shmidt condensation of propiophenone in the presence of aluminum *tert*-butoxide, followed by selective hydrogenation of the resulting 2-benzoyl-3-phenyl-2-pentene at 240–250° and a hydrogen pressure of 125 atm.

The yields and properties of the intermediate carbinols or keto olefins are summarized in Table III. The physical properties of the diphenylalkanes are given in Table IV.

Acknowledgment.—The authors express their thanks to Miss Hildegard Beck for the microanalyses.

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[7] H. Pines and W. O. Haag, *J. Am. Chem. Soc.*, **82**, 2471 (1960).

[8] The olefinic product consisted of a mixture of double bond isomers, which gave a single 1,3-diphenylalkane upon hydrogenation.