condensation of the adduct into the graduated cylinder. The product was analyzed in the same manner as described above.

Addition of HBr to Allene or Methylacetylene in the Liquid Phase.—The ultraviolet light catalyzed reactions were carried out in 100-ml. quartz tubes, which were either sealed or closed by a Teflon-tipped needle valve (obtained from Fisher and Porter Co., Clifton, N. J.) that was sealed to the top of the tube. The noninitiated reactions were carried out in Pyrex tubes which were "darkened" with a black enamel (from Krylon, Inc., Morristown, Pa.).

Allene (or methylacetylene) and HBr were condensed into the tubes at the temperature of liquid nitrogen through a vacuum system. The evacuated closed tubes were then transferred into a temperature-controlled water or "Freon" bath. A 100-W Hanau ultraviolet immersion lamp (obtained from G. W. Gates and Co., Long Island, N. Y.) was used for the initiation. If the reaction was carried out below room temperature the lamp was surrounded by a quartz mantle to insulate it against excessive cooling.

After an arbitrary period of reaction time, the tubes were transferred to a liquid nitrogen bath and opened. The unreacted gases were allowed to evaporate through a drying tube filled with anhydrous calcium sulfate ("Drierite"). The remaining adduct mixtures in the tube were slightly yellow to dark brown mobile liquids. They were analyzed as such by g.l.c. and n.m.r.

Vacuum distillation of an adduct mixture derived from the reaction of equimolar amounts of hydrogen bromide and allene produced 1,3-dibromopropane as the highest boiling component and left no residue. This indicates that, when equimolar amounts of reactants or an excess of HBr are used, telomerization is insignificant and that the g.l.c. method, therefore, can provide a complete analysis of these adduct mixtures.

The use of stringent precautions is recommended for carrying out these reactions regardless of the reaction temperature employed. In one case a vigorous explosion occurred when an equimolar mixture of allene and HBr was irradiated at room temperature for approximately 5 min. The explosion was preceded by a yellow flash in the reaction tube. In a second case a mixture containing allene, methylacetylene, and HBr in the relative molar ratios of 1:1:2 exploded when it was irradiated at −70°. In both cases the experiments were well shielded and no one was injured. The reasons for these explosions are unknown.

Acknowledgment.—The authors thank their colleague, Dr. R. B. Long, for supplying them with samples of pure allene and Miss M. Doolan for carrying out the g.l.c. analyses. The skillful technical assistance of Mr. A. M. Palmer in carrying out experiments is particularly acknowledged.

Sodium- and Potassium-Induced Reactions of β-Methylstyrene[1,2]

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Considerable difference was observed in the reactions of β-methylstyrene (I) in nonexchanging solvents in the presence of dispersed sodium or potassium. At 100–155°, in the presence of sodium, I underwent mainly dimerization to 1,5-diphenyl-4-methyl-1-pentene (V, yield 80–87%), whereas the fastest reaction in the presence of the more electropositive potassium was hydrodimerization resulting in 1,4-diphenyl-2,3-dimethylbutane (IV, optimal yield 85–93% at 80–100°). The two reactions are mechanistically different: dimerization of I is a typical carbanion-catalyzed chain reaction, whereas hydrodimerization, which probably involves the intermediate formation of an anionic free radical, is a noncatalytic reaction requiring 2 g.-atoms of metal per mole of hydrodimer formed. Dimer V underwent a slow decomposition and recombination leading to the formation of 1,3-diphenyl-2-methylpropane (III) and to a C_{11} hydrocarbon (II) to which the structure 3-methyl-4-phenylcyclobutene was assigned. The mechanism of the reaction is discussed.

It has been reported[4,5] recently that α- and β-methylstyrene react with alkylbenzenes in the presence of dispersed potassium to form 1,3-diphenylalkanes. In the case of β-methylstyrene (I) the relative rate of aralkylation was found[5] to decrease sharply with increased size of the substituent in the alkylbenzene reactant, while, simultaneously, the dimerization and concurrent hydrodimerization of I became increasingly competitive.

As an extension of the above work the reactions of I have been separately studied in nonexchanging media. Comparative experiments were carried out employing dispersed sodium or dispersed potassium as a catalyst. The effect of temperature upon the relative rate of dimerization and upon the partial evolution of the dimer into secondary products was also studied by performing the reaction in four different alkylcyclohexane solvents at their respective boiling points: cyclohexane (80°), methylcyclohexane (100°), ethylcyclohexane (132°), and isopropylcyclohexane (155°). The course of the reaction at a given temperature was followed by plotting the product composition as a function of reaction time.

The experimental procedure was similar to that described previously.[6] The reaction products were separated and analyzed by a combination of fractional distillation, gas chromatography, hydrogenation, and ozonation, as well as by infrared, ultraviolet, and n.m.r. spectroscopy. Part of the compounds formed were identified by comparison with pure synthetic samples.

Results and Discussion

As seen from Table I there is considerable difference in the composition of products obtained in the experiments with sodium and potassium catalysts.

The main dimerization product in the presence of dispersed sodium is 1,5-diphenyl-4-methyl-1-pentene (V). The dimer is obtained in high yields (80–90%) at 100° and extended reaction time (expt. 1) or at 155° and short contact time (expt. 4); the reaction under these conditions can be conveniently employed as a preparative method.

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(1) Paper XXVII of the series "Base-Catalyzed Reactions." For paper XXVI, see E. M. Lewicki, H. Pines, and N. C. Sih, *Chem. Ind.* (London), 154 (1964).

(2) This work had been supported in part by the National Science Foundation Grant G14503.

(3) On leave of absence from the Weizmann Institute of Science, Rehovoth, Israel, 1959–1961.

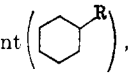
(4) J. Shabtai and H. Pines, *J. Org. Chem.*, **26**, 4225 (1961).

(5) J. Shabtai, E. M. Lewicki, and H. Pines, *ibid.*, **27**, 2613 (1962).

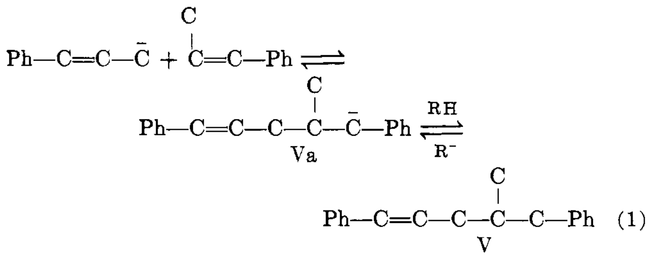
(6) H. Pines and J. Shabtai, *ibid.*, **26**, 4220 (1961).

TABLE I

COMPOSITION OF PRODUCTS OBTAINED FROM THE SODIUM- AND POTASSIUM-CATALYZED REACTIONS OF β-METHYLSTYRENE (I)

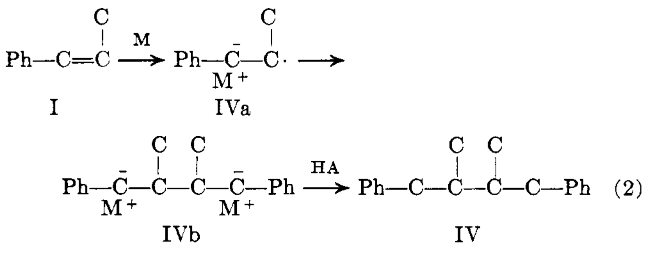
Experiment	1	2	3	4	5	6	7	8	9	10	11
Catalyst	Na	Na	Na	Na	Na	K	K	K	K	K	K
Temperature, °C.	100	132	132	155	155	80	100	100	132	155	155
Solvent (), R =	CH_3	C_2H_5	C_2H_5	i-C_3H_7	i-C_3H_7	H	CH_3	CH_3	C_2H_5	i-C_3H_7	i-C_3H_2
Reaction time,[a] hr.	5	5	8	1	5	4	1	4	4	5	9
Conversion, mole %[b]	12	63	94	77	100	4	21	43	72	100	100
Product component, wt. %											
Ph—C	1.5	1.7	2.7	0.8	1.0	...	...	...	1.0	<0.1	<0.1
Ph—C—C—C	0.3	1.2	2.6	1.2	2.7	0.5	3.0	2.6	1.7	0.2	0.2
C_{11} compound (II)[c]	3.2	5.0	6.4	0.2	1.0	...	...	...	5.8	0.1	0.1
$\mathrm{Ph{-}C{-}\overset{\overset{C}{\vert}}{C}{-}C{-}Ph}$ (III)	1.4	1.7	2.1	0.7	0.8	...	...	...	6.5	12.1	14.3
$\mathrm{Ph{-}C{-}\overset{\overset{C}{\vert}}{C}{-}\overset{\overset{C}{\vert}}{C}{-}C{-}Ph}$ (IV)	2.7	6.0	7.9	12.6	16.4	92.8	84.1	80.7	42.0	30.2	29.8
$\mathrm{Ph{-}C{=}C{-}C{-}\overset{\overset{C}{\vert}}{C}{-}C{-}Ph}$ (V)	86.5	72.6	62.8	81.0	68.0	3.0	5.4	6.7	27.8	29.5	24.9
$\mathrm{Ph{-}\overset{\overset{\overset{C}{\vert}}{\overset{C}{\vert}}}{C}{-}\overset{\overset{C}{\vert}}{C}{-}C{-}Ph}$ (VI)[d]	1.4	6.3	7.0	2.5	4.1	1.2	1.5	2.5	6.0	16.5	17.0
Higher boiling	3.0	5.5	8.5	1.0	6.0	2.5	6.0	7.5	9.2	11.4	13.7

[a] Including the time of addition of I. [b] In each experiment were used 18 g. (0.15 mole) of I, 80 g. of solvent, and 2 g. (0.087 g.-atom) of sodium or 2.2 g. (0.056 g.-atom) of potassium. [c] Assigned structure: 3-methyl-4-phenylcyclobutene (see Experimental). [d] Includes olefins with the same skeleton: expt. 1–9, 2–10%; expt. 10 and 11, 20–21%.



$$\mathrm{Ph{-}C{=}C{-}\bar{C}} + \mathrm{\overset{\overset{C}{|}}{C}{=}C{-}Ph} \rightleftharpoons \underset{\mathrm{Va}}{\mathrm{Ph{-}C{=}C{-}C{-}\overset{\overset{C}{|}}{C}{-}\bar{C}{-}Ph}} \underset{R^-}{\overset{RH}{\rightleftharpoons}} \underset{\mathrm{V}}{\mathrm{Ph{-}C{=}C{-}C{-}\overset{\overset{C}{|}}{C}{-}C{-}Ph}} \quad (1)$$

Increase in temperature or reaction time results in somewhat larger amounts of other products. It was proposed[4] that the hydrodimer IV arises from the dimerization of the alkali metal ion-radical salt IVa; the product may accumulate during the reaction in the form of the dimeric salt IVb or be converted into IV by reacting with the monomer or by the decomposition of the reaction mixture with ethanol.



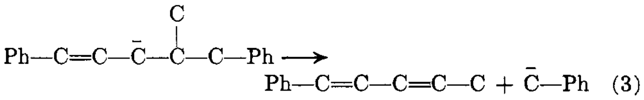
$$\underset{\mathrm{I}}{\mathrm{Ph{-}C{=}\overset{\overset{C}{|}}{C}}} \xrightarrow{M} \underset{\mathrm{IVa}}{\mathrm{Ph{-}\underset{M^+}{\bar{C}}{-}\overset{\overset{C}{|}}{C}\cdot}} \longrightarrow$$

$$\underset{\mathrm{IVb}}{\mathrm{Ph{-}\underset{M^+}{\bar{C}}{-}\overset{\overset{C}{|}}{C}{-}\overset{\overset{C}{|}}{C}{-}\underset{M^+}{\bar{C}}{-}Ph}} \xrightarrow{HA} \underset{\mathrm{IV}}{\mathrm{Ph{-}C{-}\overset{\overset{C}{|}}{C}{-}\overset{\overset{C}{|}}{C}{-}C{-}Ph}} \quad (2)$$

Reaction 2 occurs to a limited extent in the presence of sodium, but its rate relative to that of reaction 1 seems to increase somewhat with temperature (compare expt. 2 and 5).

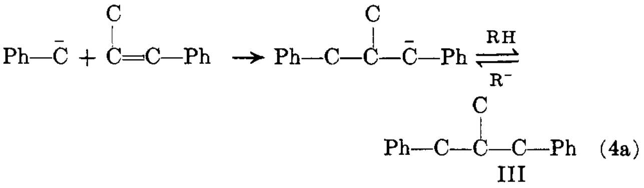
Winstein and Lapporte[7] have independently obtained compound IV from I by Conant's method,[8] which involves treatment of a β-alkylstyrene with sodium–potassium alloy in ether and subsequent quenching of the reaction mixture with alcohol.

The presence of toluene and compound II in the product indicates that V undergoes to a slight extent cleavage into a C_7 and a C_{11} unit. Such reaction can be assumed to involve metalation of V at the allylic position, followed by splitting of the resulting carbanion.



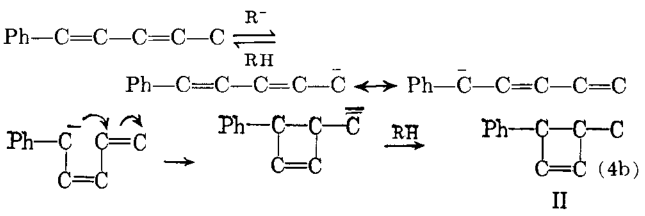
$$\mathrm{Ph{-}C{=}C{-}\bar{C}{-}\overset{\overset{C}{|}}{C}{-}C{-}Ph} \longrightarrow \mathrm{Ph{-}C{=}C{-}C{=}C{-}C} + \mathrm{\bar{\underline{C}}{-}Ph} \quad (3)$$

The benzyl carbanion obtained can form toluene by proton abstraction or react with β-methylstyrene to give 1,3-diphenyl-2-methylpropane (III).[5]



$$\mathrm{Ph{-}\bar{C}} + \mathrm{\overset{\overset{C}{|}}{C}{=}C{-}Ph} \rightarrow \mathrm{Ph{-}C{-}\overset{\overset{C}{|}}{C}{-}\bar{C}{-}Ph} \underset{R^-}{\overset{RH}{\rightleftharpoons}} \underset{\mathrm{III}}{\mathrm{Ph{-}C{-}\overset{\overset{C}{|}}{C}{-}C{-}Ph}} \quad (4a)$$

On the other hand the phenylpentadiene produced can polymerize into high boiling products or it can undergo cyclization and form compound II by the following mechanism.



Support for the proposed formation of phenylpentadiene as a precursor of II was obtained by a separate experiment. A reaction was carried out exactly under the conditions of expt. 9 and about 90 min. after completing the addition of I, 1-phenyl-1,3-pentadiene (1.44 g., 0.01 mole) was injected in the reacting mixture. The yield of II increased from 5.8%

[7] S. Winstein, private communication.
[8] J. B. Conant and A. H. Blatt, *J. Am. Chem. Soc.*, **50**, 551 (1928).

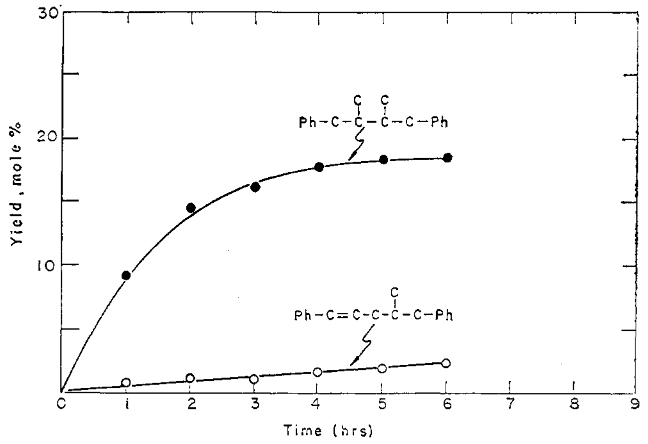


Fig. 1.—Relative rate of formation of 1,5-diphenyl-4-methyl-1-pentene and 1,4-diphenyl-2,3-dimethylbutane from β-methylstyrene, at 100°, in the presence of potassium.

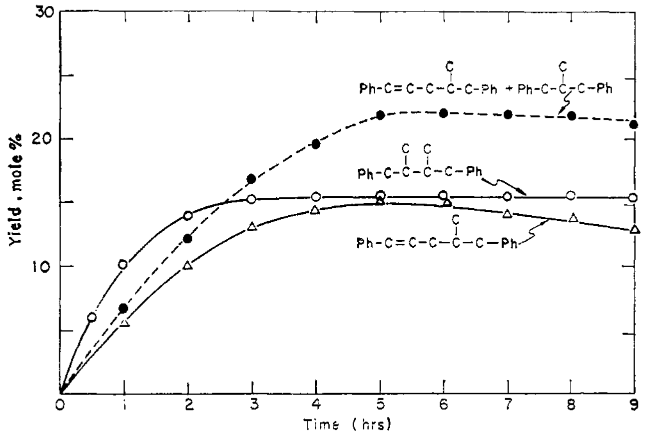


Fig. 2.—Relative rate of dimerization and hydrodimerization of β-methylstyrene at 155°, in the presence of potassium; formation of (a) 1,5-dipenyl-4-methyl-1-pentene (V); (b) 1,4-diphenyl-2,3-dimethylbutane (IV); and (c) IV + 1,3-diphenyl-2-methylpropane (III).

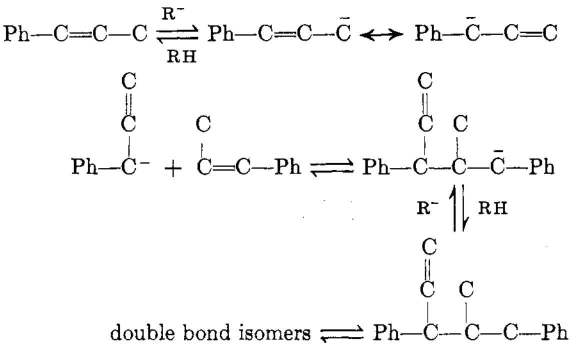
(expt. 9) to 9.1%, corresponding to a 40% transformation of the diene into compound II.

The formation of high boiling material is probably accompanied to some extent by hydride-transfer reactions[6] as indicated by the presence of small amounts of *n*-propylbenzene.

$$\mathrm{Ph{-}C{=}C{-}C} \underset{-\mathrm{H}^-}{\overset{\mathrm{H}^-}{\rightleftharpoons}} \mathrm{Ph{-}\bar{C}{-}C{-}C} \underset{\mathrm{R}^-}{\overset{\mathrm{RH}}{\rightleftharpoons}} \mathrm{Ph{-}C{-}C{-}C} \quad (5)$$

On the other hand, *n*-propylbenzene has been shown[5] to react with β-methylstyrene with the formation of compound VI. Olefins possessing the skeleton of VI (footnote *d*, Table I) may result by hydride transfer reaction of the intermediate carbanion (Ph—C(C_2)-C(C)—$\bar{C}$—Ph). A second possibility, however, is that dimerization of I occurs to some extent by a path different from reaction 1; the carbanion derived from I in the initiation step may react as a "benzylic" rather than an "allylic" carbanion.

In the presence of dispersed potassium, between 80–100° (Table I, expt. 6–8), hydrodimerization of I (reaction 2) is strongly predominant. This probably depends on the stronger electropositive character of potassium. In the presence of potassium the rate of formation of the anionic free radical IVa followed by dimerization (reaction 2) is much faster than the rate-determining step of reaction 1.



(6)

Figure 1 shows that at 100° the relatively much faster reaction 2, producing hydrodimer IV, reaches a standstill after about 4 hr., although the total conversion of I at this point is less than 50%. On the other hand, the slow reaction 1 continues normally beyond this point. At 155° (Fig. 2) reaction 1 becomes increasingly competitive, but otherwise the pattern is preserved. Reaction 2 is practically stopped after 2.5 hr., whereas reaction 1 continues and compound V reaches a maximum concentration after about 5 hr. The decrease in the concentration of V at longer contact time is obviously due to the splitting reaction 3. Since the benzyl carbanion, produced by this cleavage, reacts almost quantitatively with I to form compound III, the latter can serve as a measure of the amount of the dimer consumed in the secondary reaction. It is seen (Fig. 2, dotted line) that, if compound III is taken into account, the total yield of V after 5 hr. (21.9 mole %) is actually larger than that of the hydrodimer IV (15.3 mole %).

The observed change in the relative rate of the competing hydrodimerization and dimerization reactions at longer contact time can be explained by considering the mechanistically different character of reactions 1 and 2.

Reaction 2, which involves the formation and dimerization of an anionic free radical, is a noncatalytic reaction requiring 2 g.-atoms of potassium per mole of hydrodimer formed. Calculations on this basis show that in all experiments in the presence of potassium the total molar amount of hydrodimer formed approaches but does not exceed the required double gram-atomic amount of potassium. Thus, with 2.2 g. (0.056 g.-atom) of potassium employed in each experiment, the total amounts of hydrodimer, after completion of reaction 2, are as follows (mole): expt. 8, 0.026; expt. 9, 0.023; expt. 11, 0.023. (In the low conversion expt. 6 and 7, reaction 2 is not completed and the amount of hydrodimer is consequently lower than calculated.) It is, therefore, obvious that the interruption of the fastest reaction 2 corresponds to the point of nearly complete consumption of all the metallic potassium available.

Reaction 1, on the other hand, is a typical carbanion-catalyzed chain reaction, which requires only a small amount of potassium for producing the initiating species (R^-K^+). This reaction, therefore, continues to proceed uninterrupted even after the metallic potassium has been gradually consumed in the formation of compound V.

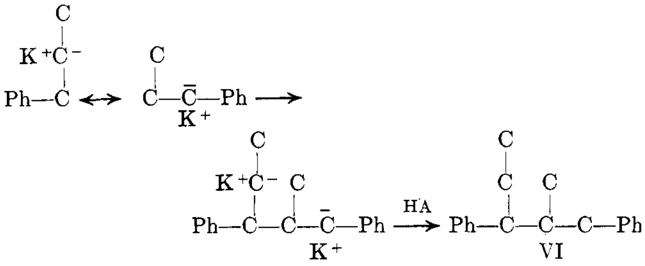
The following phenomena are also observed in the presence of potassium (Table I, expt. 6–11).

Compound I reacts at a low rate, even at 80° (expt. 6), whereas practically no reaction is observed at this temperature in the presence of sodium. At 80–100° no toluene or compounds II and III are present in the product. This is obviously due to the very low rate of formation of V at this temperature and to the absence of the secondary reactions 3 and 4, which are based on V as a precursor.

At 132° (expt. 9), owing to the increase in amount of V, reactions 3 and 4 do take place as indicated by the appearance of compounds II and III. It should be noted that this temperature is optimal for the formation of compound II, both in the presence of potassium or sodium.

At 155° (expt. 10), the toluene and compound II seem to be involved in further reaction. Toluene is almost completely consumed in reaction 4a, giving increased amounts of compound III, whereas II is obviously unstable at this temperature and is converted into high boiling products. It has been shown recently[9] that cyclobutenes substituted in the allylic position undergo easy thermal splitting. Thus, 3-methylcyclobutene is cleaved at the biallylic (3,4-) position to give 1,3-pentadiene already at 160°. In the present case compound II can probably likewise undergo thermal splitting to an open-chain diene, which may then polymerize under the experimental conditions.

The increase in the amount of compound VI at 155° may be due to an increase in the extent of the hydride transfer reaction 5 with temperature. It is not excluded, however, that a part of VI results from hydrodimerization of I by a path alternative to reaction 2.



On the other hand, the increase in the amount of olefins having the skeleton of VI (Table I, footnote *d*) indicates that reaction 6 increases somewhat in importance under these conditions. It is seen, therefore, that both the dimerization and hydrodimerization of I proceed in a somewhat less selective manner in the presence of potassium at 155°.

Experimental

Apparatus and Procedure.—The apparatus consisted essentially of a three-necked flask, provided with a high speed (7500 r.p.m.) stirrer and a sampling device, permitting the withdrawal of small liquid samples (~0.1 ml.) during the reaction.

The experiments were carried out under a slow stream of dry helium. In each case, the proper alkylcyclohexane, 20 g., was introduced in the flask and to this was added sodium, 2 g. (or potassium, 2.2 g.), freshly cut under the same solvent. The mixture was then brought to boiling and stirred for 45–60 min. Another portion of the solvent, 40 g., was added slowly (30 min.) and the mixing continued for 1 hr. To the fine, white-colored dispersion obtained was added dropwise (1 hr.) a solution of I (18 g.) in the same alkylcyclohexane (20 g.). I was >99% pure and contained 35% of the *cis* and 65% of the *trans* isomer. The color of the dispersion turned immediately brown and later deep brown or black. No promoter was employed in any of the experiments as the quick change in color indicated that compound I itself immediately provides the necessary initiating species. Samples of the reacting mixture were withdrawn every 15–30 min. and, after treatment with ethanol, examined by gas chromatography.

The final product was cooled to 0–5° and the catalyst decomposed with ethanol. The solution obtained was washed with 10% aqueous hydrochloric acid, followed by 10% aqueous sodium bicarbonate, dried, and the solvent removed at 100 mm.

Identification of Reaction Products. 1,4-Diphenyl-2,3-dimethylbutane (IV).—This compound was isolated in about 99% purity by fractional distillation of the product formed at 100° in the presence of potassium (expt. 8). It had b.p. 118–122° (0.5 mm.), n^{20}_{D} 1.5455, and was later shown by gas chromatography to consist of a nearly equimolar mixture of the *erythro* and *threo* isomers; the retention volumes of the two components, relative to *n*-hexylbenzene, were isomer I, 9.2, and isomer II, 10.0 (14-ft. column, filled with 8% silicon oil on Chromosorb; helium flow rate 40 ml./min.; temperature 200°).

Anal. Calcd. for $C_{18}H_{22}$: C, 90.67; H, 9.31. Found: C, 90.89; H, 9.15.

Compound IV did not contain any olefinic unsaturation and showed the following infrared absorption maxima (in cm.$^{-1}$; intensity: s, strong; m, medium; w, weak): 698 (s), 733 (s), 746 (s), 785 (w), 798 (w), 845 (w), 912 (w), 1037 (m), 1071 (w), 1103 (w), 1116 (w), 1162 (w), 1185 (w), 1365 (w), 1388 (m), 1462 (s), 1502 (s), 1615 (m), 1712 (w), 1750 (w), 1815 (w), 1884 (w), 1963 (w), 2900 (w), 2950 (s), 2980 (s), 3065 (s), 3100 (w).

The mass spectra[7] of IV showed that the compound has mol. wt. 238. Also, in agreement with the assigned structure, the n.m.r. spectrum of IV indicated that the sum of benzylic and tertiary hydrogen atoms (six) is equal to the sum of methyl hydrogens.

The structure of compound IV was conclusively established by comparison with a sample of *erythro*- and *threo*-1,4-diphenyl-2,3-dimethylbutane, synthesized by independent means (see below). The compared hydrocarbons showed identical retention volumes and infrared and n.m.r. spectra.

1,5-Diphenyl-4-methyl-1-pentene (V).—This compound was isolated in a pure form (>99%) by fractional distillation of the product obtained at 132° in the presence of sodium. It had b.p. 140–141° (0.55 mm.), n^{20}_{D} 1.5710, and contained a phenyl-conjugated double bond as determined by ultraviolet analysis [λ_{max} 2500 Å., (ϵ 14,300)] and semimicro hydrogenation.

Anal. Calcd. for $C_{18}H_{20}$: C, 91.46; H, 8.54. Found: C, 91.35; H, 8.50.

The product of hydrogenation of V was identified as 1,5-diphenyl-2-methylpentane by comparison of its infrared spectrum and retention volume with those of a synthetic sample. After establishing the skeleton of V, the position of the double bond was determined by ozonation.

The dimer, 1.5 g., was dissolved in carbon tetrachloride, 30 ml., and ozonized at −20° for 2 hr. After removing most of the solvent, the ozonide was decomposed by boiling with 30 ml. of a solution consisting of equal volumes of 10% aqueous sodium bicarbonate and 30% hydrogen peroxide. The acid product obtained (1.65 g., 96% of theoretical) was purified by sublimation at 0.5 mm. and identified by gas chromatography (see Analytical) as a nearly equimolar mixture of benzoic and γ-phenylisovaleric acid.

Compound II.—The structure of 3-methyl-4-phenylcyclobutene was assigned to this hydrocarbon, which was isolated in nearly 99% purity by fractional distillation of the combined products of several experiments carried out at 132° in the presence of potassium (expt. 9). It had b.p. 143° (60 mm.), n^{20}_{D} 1.5340.

Anal. Calcd. for $C_{11}H_{12}$: C, 91.60; H, 8.40. Found: C, 91.48; H, 8.55.

Compound II contained one double bond as determined by semimicro hydrogenation. The ultraviolet spectrum [λ_{max} 2480 Å. (ϵ 1,380)] showed that the double bond is not conjugated with the benzene ring; the absorption maxima, however, appears at a shorter wave length, whereas the molecular extinction is some-

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(9) E. Gil-Av and J. Shabtai, *J. Org. Chem.*, **29**, 257 (1964).

what higher compared to that of aromatic olefins with an open side chain.[10]

Evidence for the presence of a cyclobutene ring in II was provided by the infrared spectrum, which showed the following adsorption maxima (in cm.$^{-1}$; intensity: s, strong; m, medium; w, weak): 668 (w), 700 (s), 834 (w), 844 (w), 868 (m), 891 (m), 927 (w), 966 (w), 1002 (m), 1012 (m), 1037 (m), 1077 (m), 1138 (w), 1163 (w), 1188 (w), 1241 (w), 1271 (w), 1376 (e), 1461 (s), 1491 (w), 1508 (s), 1540 (w), 1575 (w), 1600 (w), 1612 (s), 1754 (w), 1813 (w), 1880 (w), 1960 (w), 2900 (m), 2970 (s), 3070 (m), 3130 (m).

As seen, the =C—H stretching absorption appears at 3130 cm.$^{-1}$, which is characteristic[11] for a cyclobutene without a substituent at the double bond (cyclobutene,[11] 3126 cm.$^{-1}$; 3-methylcyclobutene,[9] 3130 cm.$^{-1}$). Also, typically for a strained four-membered ring[11] the C=C stretching frequency is very low (1575 cm.$^{-1}$), as found in cyclobutene (1565 cm.$^{-1}$) and 3-methylcyclobutene (1566 cm.$^{-1}$). It is significant that apart from the band at 1575 cm.$^{-1}$ the spectrum of II contains a second weak band at 1600 cm.$^{-1}$, which is also observed in the spectrum of 3-methylcyclobutene.[9] The well-defined doublet exhibited by the latter compound (1566–1600 cm.$^{-1}$) seems to be characteristic for cyclobutenes with an alkyl or aryl substituent in the 3 position; a similar doublet has been observed at higher frequencies in the spectra of 3-alkylcyclopentenes[12] (1616–1650 cm.$^{-1}$) and 3-alkylcyclohexenes[13] (1650–1685 cm.$^{-1}$). The specific absorption pattern[14] in the 1700–2000-cm.$^{-1}$ range and the strong band at 700 cm.$^{-1}$ show that the benzene ring in II is monosubstituted.

Ozonation of II under the above conditions (see compound V) gave as the sole product (yield, 94%) a semisolid acid, which failed to crystallize from a number of solvents, including carbon tetrachloride. The acid contained two carboxylic groups, as determined by neutralization in alcoholic solution, and analyzed for the expected α-methyl-α'-phenylsuccinic acid.

Anal. Calcd. for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.20; H, 5.94.

Sources and Synthesis of Pure Hydrocarbons.—1,3-Diphenyl-2-methylpropane (III) and **1,3-diphenyl-2-methylpentane (VI)** were available from previous work.[15] **1-Phenyl-1,3-pentadiene** was synthesized by N. C. Sih of our laboratory.

1,5-Diphenyl-2-methylpentane.—This compound was synthesized through the Grignard reaction of 1-bromo-3-phenylpropane with phenyl-2-propanone. The intermediate carbinol, **1,5-diphenyl-2-methyl-2-pentanol**, b.p. 213–214° (18 mm.), $n^{20}D$ 1.5568, was obtained in 64% yield. It was dehydrated over Harshaw alumina[15] at 330–340° and the resulting mixture of two double-bond isomers was hydrogenated at 150° and 120-atm. hydrogen pressure over chromia–alumina. After distillation the obtained 1,5-diphenyl-2-methylpentane was 99% pure, b.p. 126–127° (0.4 mm.), $n^{20}D$ 1.5413.

Anal. Calcd. for $C_{18}H_{22}$: C, 90.65; H, 9.31. Found: C, 90.53; H, 9.35.

1,4-Diphenyl-2,3-dimethylbutane (IV).—This compound was obtained by reacting an ethereal solution of 1-phenyl-2-chloropropane at reflux temperature with magnesium turnings. The chloride was prepared by reacting 1 mole of 1-phenyl-2-propanol dissolved in 1 mole of pyridine with 1.3 moles of thionyl chloride.

The 1,4-diphenyl-2,3-dimethylbutane obtained consisted of a 40:60% mixture of *erythro* and *threo* isomers, having retention times identical with the compound IV obtained from the dimerization of β-methylstyrene.

Analytical.—Preparative fractional distillation of reaction products was carried out at reduced pressure on a 20 cm. × 12 mm. column, filled with stainless steel wire gauze packing, or when necessary (*e.g.*, in the isolation of compound II) on a Piros–Glover spinning band column.

Quantitative analyses of product components, as well as of hydrogenation or ozonation products, were carried out by gas chromatography on a programmed temperature apparatus (F and M, Model 300). Several types of columns were used including (a) a 9-ft. column, filled with 10% silicone gum rubber on Chromosorb P; and (b) a 14-ft. column with 8% silicone (DC 550 fluid) on the same support. In the analysis of acids the liquid phase was silicone, containing 10% stearic acid.

N.m.r. spectra were measured on a Varian spectrometer.

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Synthesis of 1-Butene-2,4-sultam

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The chlorosulfonylation of 1,4-dichlorobutane has been effected in refluxing sulfur dioxide solution to give 1,4-dichlorobutane-2-sulfonyl chloride. The latter has been converted to 4-chloro-1-butene-2-sulfonamide by treatment with triethylamine and ammonia, and the chlorobutenesulfonamide has been cyclized to 1-butene-2,4-sultam by treatment with alcoholic alkali. The sultam is a colorless, uncrystallizable oil which darkens on exposure to air and polymerizes on distillation at reduced pressure. Its crystalline N-benzenesulfonyl derivative melted at 134–135°. The sultam polymerized by Michael addition in the presence of strong base, giving a water-insoluble solid, m.p. 170–190°, $[\eta]$ 0.08 dl./g. Preliminary investigation has indicated that the sultam can also polymerize by radical-initiated olefin addition and by sustained ring opening.

In a general study of the preparation and polymerization of aliphatic sultams,[2] we have examined the effect of an exocyclic double bond on the reactivity of the five-membered sultam ring. Although the literature contains no examples of simple methylene-substituted sultams, it seemed reasonable to suppose the chlorosulfonylation[3] of aliphatic dihalides would afford a synthetic route to unsaturated sultams by the transformations indicated below for the preparation of 1-butene-2,4-sultam (I).[4]

The attempted chlorosulfonylation of II by the method successfully applied to 1-chlorobutane by

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[2] (a) A. D. Bliss, W. K. Cline, C. E. Hamilton, and O. J. Sweeting, *J. Org. Chem.*, **28**, 3537 (1963); (b) A. D. Bliss, W. K. Cline, C. E. Hamilton, and O. J. Sweeting, *J. Polymer Sci.*, to be published.

[3] C. F. Reed, U. S. Patent 2,046,090 (June 30, 1936); *Chem. Abstr.*, **30**, 5593 (1936).

[4] We have followed the common practice of naming sultams as derivatives of the longest hydrocarbon chain to which both sulfur and nitrogen are attached [B. Helferich, K. Geist, and H. Plümpe, *Ann.*, **651**, 17 (1962), *q.v.*] rather than by the cumbersome and seldom-used heterocyclic nomenclature suggested in "The Naming and Indexing of Chemical Compounds from Chemical Abstracts," American Chemical Society, 1962, in which I would be named 5-methyleneisothiazolidine 1,1-dioxide.