

could be recovered. Acidification of the strongly alkaline filtrates (pH 13) gave carbon dioxide, hydrogen sulfide, and thiophene-3-carboxylic acid (25 g.), m.p. 137–138°, lit.<sup>23</sup> m.p. 138.4°. The

ether extracts of the acidified filtrates gave additional thiophene-3-carboxylic acid (7 g.), m.p. 137–138°, for a total yield of 82% (32 g., 0.25 mole). The melting point of the acid was undepressed when mixed with an authentic sample. The oxidation results were independent of the excess sodium dichromate employed (0–64% excess).

(23) E. Campaigne and W. LeSeur, *J. Am. Chem. Soc.*, **70**, 1555 (1948).

## The Alkali Metal Catalyzed Reactions of $\omega$ -Phenyl-1-alkenes. The Novel Cyclizations of 6-Phenyl-1-hexene and 7-Phenyl-1-heptene<sup>1,2</sup>

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The catalytic conversion of 6-phenyl-1-hexene and 7-phenyl-1-heptene in the presence of alkali metal-organometal catalysts has been investigated. The potassium- and cesium-catalyzed reactions afforded a substantial amount of intramolecular cyclization; sodium caused primarily double-bond migrations, while butyllithium exerted no catalytic effect. In potassium- and cesium-catalyzed reactions, 6-phenyl-1-hexene produced mainly *cis*- and *trans*-1-methyl-2-phenylcyclopentane and 1,2,3,3a,8,8a-hexahydrocyclopent[*a*]indene. 7-Phenyl-1-heptene yielded mostly *cis*- and *trans*-1-methyl-2-phenylcyclohexane and 1,2,3,4,4a,9a-hexahydrofluorene.

The sodium- and potassium-catalyzed side-chain alkylation, alkenylation, and aralkylation by olefins of alkyl aromatic hydrocarbons having a benzylic hydrogen have been the subject of extensive study in our laboratory.<sup>1,5</sup> For example, when toluene was used as an alkyl aromatic, its alkylation by ethylene gave mainly *n*-propylbenzene and 3-phenylpentane,<sup>6</sup> its alkenylation by isoprene yielded both 1-phenyl-3-methylpentene and 1-phenyl-4-methylpentene,<sup>7</sup> and its aralkylation by styrene produced 1,3-diphenylpropane.<sup>8</sup> The formation of the majority of products from these base-catalyzed reactions is explained *via* a carbanion mechanism.<sup>5</sup>

In order to further the understanding of the base-catalyzed reactions, the present investigation has been extended to include  $\omega$ -phenyl-1-alkenes which contain both intrinsic acidic benzylic hydrogens and double bonds.

The reactions of 6-phenyl-1-hexene and 7-phenyl-1-heptene will be discussed in the present paper. Their intramolecular alkylations (cyclization) seem to be plausible owing to the close proximity of the benzylic carbon to the terminal double bond. The success of this type of cyclization depends largely on the relative rate of intramolecular alkylation against those of the competing reactions, such as isomerization of the double bond, hydride addition, intermolecular alkylation, etc. Cyclization which necessitates a special molecular orientation is usually attended by a negative entropy of activation, and therefore generally is a less favorable reaction.

The next paper of this series will describe the reactions of 4-phenyl-1-butene and 5-phenyl-1-pentene

which were investigated to determine what products would be obtained in a system where ring formation was unfavored.

Alkali metals *per se* are not the catalysts and it is necessary to use a chain initiator, such as anthracene, *o*-chlorotoluene, etc., for the reaction to occur. These initiators usually react readily with alkali metals to give organoalkali metal compounds which initiate the reaction. The relative behaviors of the alkali metals as alkylation (or alkenylation or aralkylation) catalysts<sup>9</sup> have been compared in only a few instances.<sup>5,10,11</sup> Therefore the effect of lithium, sodium, potassium, and cesium upon the reaction was also investigated.

### Discussion of Results

The reactions of  $\omega$ -phenyl-1-alkenes, initiated by *o*-chlorotoluene,<sup>12</sup> were carried out at the refluxing temperature (about 185°) of an inert solvent, such as *n*-butylcyclohexane or *sec*-butylcyclohexane, in the presence of an alkali metal-organometal catalyst under the experimental conditions give in Table I.

The rate of conversion of  $\omega$ -phenyl-1-alkenes was found to be dependent largely on how the catalyst was prepared. In various runs using the same metal as catalyst, the required reaction times differed, but, nevertheless, the product distributions remained nearly the same. Therefore the product distribution may be considered as a measure of the catalytic character of different alkali metals.

**I. 6-Phenyl-1-hexene.**—The composition of products obtained from this reaction is summarized in Table II (see Scheme I). Hydride addition and double bond migration are the two most common reactions of olefins brought about by alkali metal catalysis.<sup>5</sup> In the present study, the production of *n*-hexylbenzene (2) either from the parent olefin 1 or from its isomers (3,

(1) Paper XXIX of the series, "Base-Catalyzed Reactions." Paper XXVIII: H. Pines and N. C. Sih, *J. Org. Chem.*, **30**, 280 (1965).

(2) This work was supported in part by a National Science Foundation Grant NSF-G 14503.

(3) To whom inquiries should be made.

(4) Taken in part from the Ph.D. Thesis of N. C. Sih, Northwestern University, June 1964.

(5) For literature references, see H. Pines and L. Schaap, *Advan. Catalysis*, **12**, 116 (1960).

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

(7) See ref. 1, paper XXVIII of this series.

(8) H. Pines and D. Wunderlich, *J. Am. Chem. Soc.*, **80**, 8001 (1958).

(9) The actual catalyst is alkali metal-organometal. The term, "base" or "alkali metal," is used throughout this paper as catalyst for simplicity.

(10) L. Schaap and H. Pines, *J. Am. Chem. Soc.*, **79**, 4967 (1957).

(11) The "size effect" of alkali metal ions was related to the product distribution of monoadducts in pentylation of arenes. See paper XXVIII of this series (ref. 1).

(12) H. Gilman and H. A. Pacevitz, *J. Am. Chem. Soc.*, **62**, 673 (1940).

TABLE I  
 REACTION CONDITIONS FOR  $\omega$ -PHENYL-1-ALKENES<sup>a</sup>

Expt.	Catalyst (g.-atom)	Alkene, mole	<i>o</i> -Chlorotoluene, mole	Solvent, mole	Reactn. time, hr.	% conversion
6-Phenyl-1-hexene						
1	<i>n</i> -BuLi ( $1 \times 10^{-2}$ )	$2 \times 10^{-2}$	0	$2 \times 10^{-2b}$	9.5	0
2	Na ( $2.5 \times 10^{-2}$ )	$5.0 \times 10^{-2}$	$5.0 \times 10^{-3}$	$8.6 \times 10^{-2c}$	6.5	100
3	K ( $2.5 \times 10^{-2}$ )	$5.0 \times 10^{-2}$	$5.0 \times 10^{-3}$	$8.6 \times 10^{-2c}$	18.5	100
4	Cs ( $1.1 \times 10^{-2}$ )	$2.2 \times 10^{-2}$	$2.2 \times 10^{-3}$	$8.6 \times 10^{-2b}$	15	66.8
7-Phenyl-1-heptene						
5	Na ( $2.3 \times 10^{-2}$ )	$4.6 \times 10^{-2}$	$4.6 \times 10^{-3}$	$4.6 \times 10^{-2c}$	4.5	100
6	K ( $6.0 \times 10^{-2}$ )	$1.2 \times 10^{-1}$	$1.2 \times 10^{-2}$	$1.2 \times 10^{-1c}$	12.5	92.6
7	Cs ( $1.8 \times 10^{-2}$ )	$3.6 \times 10^{-2}$	$3.6 \times 10^{-3}$	$1.1 \times 10^{-2b}$	0.5	100

<sup>a</sup> Reaction temperature, about 185°. <sup>b</sup> *sec*-Butylcyclohexane. <sup>c</sup> *n*-Butylcyclohexane.

etc.) was evidence of the former reaction. The isomerization of the double bond through an allylic carbanion **1a** to give 6-phenyl-*x*-hexenes (**3**, etc.) was an illustration of the latter. *trans*- and *cis*-1-methyl-2-phenylcyclopentane (**4** and **5**), 1,2,3,3a,8,8a-hexahydrocyclopent[*a*]indene (**6**), phenylcyclohexane (**7**), and biphenyl (**8**) were produced by the cyclization of the benzylic carbanion **1c**. The favored formation of compounds **4** and **5** over compound **7** (detected only with cesium catalyst) can be rationalized from the stabilities of their carbanion intermediates (**4a** and **5a** vs. **7a**; *i.e.*, primary greater than secondary). From the apparent equilibrium ratio, *trans/cis* = 5.0–5.1, the *cis*-1-methyl-2-phenylcyclopentane (**5**) must be about 1.5 kcal./mole (at 185°) higher in energy than the *trans* isomer **4**. Compound **8** was a secondary product resulting from the dehydrogenation<sup>9</sup> of compound **7**. The further cyclization of **5a** yielded compound **6**. An analogous reaction in which a carbanion alkylated an aromatic ring was observed previously in the potassium-catalyzed ethylation of aromatics leading to the formation of indans.<sup>10</sup>

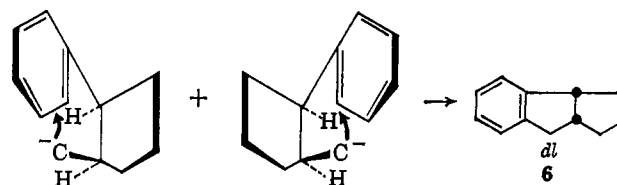
TABLE II

THE COMPOSITION OF PRODUCTS FROM 6-PHENYL-1-HEXENE

Product	Catalyst				
	<i>n</i> -BuLi	Na	K <sup>a</sup>	K <sup>b</sup>	Cs
	Mole %				
Toluene <sup>c</sup>	...	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>
<i>n</i> -Hexylbenzene ( <b>2</b> )	Trace (?)	4.5	4.3	4.7	9.1
6-Phenyl- <i>x</i> -hexenes ( <b>3</b> , etc., <i>x</i> = 2, 3, 4)	Trace	85.0	14.0	13.2	25.8
<i>trans</i> -1-Methyl-2-phenylcyclopentane ( <b>4</b> )	0	3.5	48.0 <sup>e</sup>	49.6 <sup>e</sup>	37.1 <sup>e</sup>
<i>cis</i> -1-Methyl-2-phenylcyclopentane ( <b>5</b> )	0	6.4	9.4 <sup>e</sup>	9.7 <sup>f</sup>	7.4 <sup>e</sup>
1,2,3,3a,8,8a-Hexahydrocyclopent[ <i>a</i> ]indene ( <b>6</b> )	0	0	10.6	11.4	18.2
Phenylcyclohexane ( <b>7</b> )	0	0	0	0	2.5
Biphenyl ( <b>8</b> )	0	0	0	0	Trace
Others <sup>h</sup>	0	0.6	13.7	11.4	0

<sup>a</sup> Reaction time, 18.5 hr. <sup>b</sup> Reaction time, 26.75 hr. <sup>c</sup> Originated from the initiator, *o*-chlorotoluene. <sup>d</sup> Detected. <sup>e</sup> *trans/cis* = 5.1. <sup>f</sup> *trans/cis* = 5.1. <sup>g</sup> *trans/cis* = 5.0. <sup>h</sup> Mostly high boilers.

Stereochemically, the 3a and 8a hydrogens in compound **6** are likely to be *cis* to each other owing to the rigidity of the bicyclo[3.3.0]octane system, in which the *cis* form has been found to have about 6 kcal./mole lower energy than the *trans* form.<sup>13</sup> Compounds **4**, **5**, and **6** are expected to be racemates. The configurations of the *trans*- and *cis*-1-methyl-2-phenylcyclopentanes were assigned on the basis of chemical evidence and physical data. They were synthesized by a Grignard reaction followed by dehydration and catalytic hydrogenation. According to Cram's rule,<sup>14</sup> the major product from the reaction of 2-methylcyclopentanone with phenylmagnesium bromide should be *trans*-1-phenyl-2-methylcyclopentanol. The *cis* dehydration<sup>15</sup> of this alcohol by phosphorus oxychloride-pyridine (to 1-phenyl-5-methylcyclopentene) and subsequent catalytic hydrogenation (*cis* addition of hydrogen to the double bond from the less hindered side<sup>16</sup>) should result in the preferential formation of *cis*-1-methyl-2-phenylcyclopentane, *cis/trans* = 2.8. From another synthetic route, the 1-methyl-2-phenylcyclopentanes, obtained *via* acid dehydration of the alcohol by potassium bisulfate (to give mainly "the most substituted"<sup>17</sup> 1-phenyl-2-methylcyclopentene) followed by catalytic hydrogenation,<sup>16</sup> had a *cis/trans* ratio of 7.7. The pure *cis* isomer was found to have a higher boiling point and higher refractive index than the *trans* isomer (*cis*,  $n_{D}^{20}$  1.5246; *trans*,  $n_{D}^{20}$  1.5162), in agreement with von Auwers-Skita rule.<sup>18</sup>



II. 7-Phenyl-1-heptene.—The experimental reaction conditions used for 7-phenyl-1-heptene are presented in Table I, while the products obtained are given in Table III. The formations of *n*-heptylbenzene (**10**), 7-phenyl-*x*-heptenes (**11**, etc.), *trans*- and *cis*-1-methyl-2-phenylcyclohexane (**12** and **13**), and 1,2,3,4,4a,9a-hexahydrofluorene (**14**) are shown in Scheme II. 8-Methyl-1,2,3,3a,8,8a-hexahydrocyclopent[*a*]indene (**16**) probably originates from the reactive secondary carbanion **15a** (see Scheme II). The stereochemistry of compounds **12** and **13** (**12**, *trans*,  $n_{D}^{20}$  1.5170; **13**, *cis*,  $n_{D}^{20}$  1.5277) was based on arguments previously described for compounds **4**

(14) D. J. Cram and F. A. Abd Elhafez, *J. Am. Chem. Soc.*, **74**, 5828, 5835 (1952).

(15) S. Gredschmidt and W. C. Veer, *Rec. trav. chim.*, **67**, 489 (1948).

(16) (a) R. L. Burwell, *Chem. Rev.*, **57**, 895 (1957); (b) M. Cardew and R. L. Burwell, *J. Am. Chem. Soc.*, **82**, 6289 (1960).

(17) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., Inc., New York, N. Y., 1959, pp. 473–476.

(18) (a) K. von Auwers, *Ann.*, **420**, 84 (1920); (b) A. Skita, *ibid.*, **56**, 1014 (1923).

(13) J. W. Barrett and R. P. Linstead, *J. Chem. Soc.*, 611 (1936).

## SCHEME I

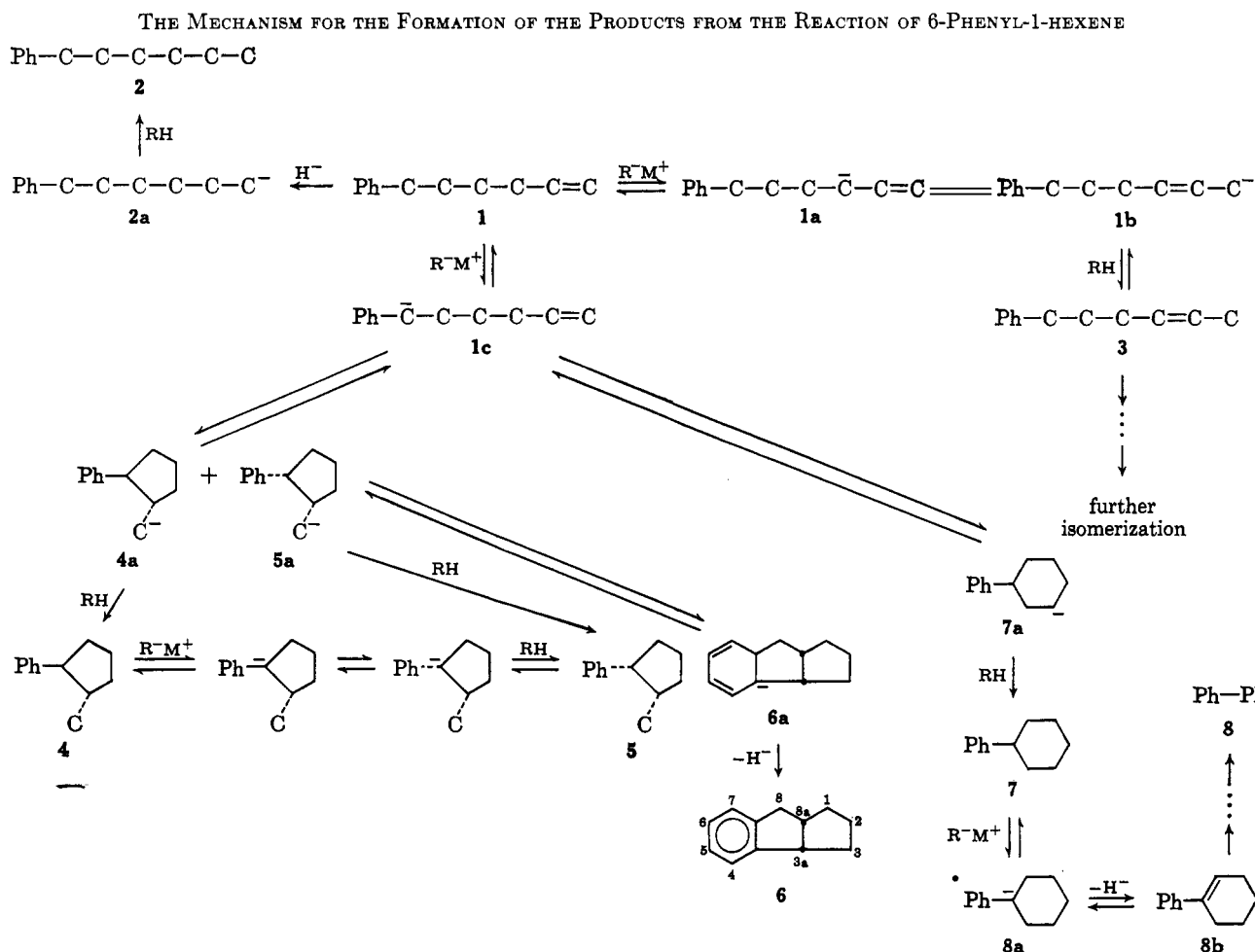


TABLE III

THE COMPOSITION OF PRODUCTS FROM 7-PHENYL-1-HEPTENE

Product	Catalyst		
	Na	K	Cs
	Mole %		
Toluene <sup>a</sup>	b	b	b
<i>n</i> -Heptylbenzene (10)	50.2	10.2	11.4
7-Phenyl- <i>x</i> -heptenes (11, etc., $x = 2, 3, 4, 5$ )	...	11.2	2.5
<i>trans</i> -1-Methyl-2-phenylcyclohexane (12)	3.8	39.0	35.0
<i>cis</i> -1-Methyl-2-phenylcyclohexane (13)	2.1	28.6	18.6
1,2,3,4,4a,9a-Hexahydrofluorene (14)	1.1	5.9	6.7
8-Methyl-1,2,3,3a,8,8a-hexahydrocyclopent[ <i>a</i> ]indene (16)	0	~0.7	1.1
Phenylcycloheptane (17)	0	0	0
Others <sup>c</sup>	42.8	4.4	24.7

<sup>a</sup> Originated from the initiator. <sup>b</sup> Detected. <sup>c</sup> Mostly high boilers.

and 5. A mixture of 1-methyl-2-phenylcyclohexanes synthesized *via* acid dehydration had a *cis/trans* ratio of 7.3. The configuration of the 4a and 9a hydrogens in compound 14 could not be assigned, since the *trans* isomer of a 5-6 fused ring system has a lower heat of combustion than its *cis* form by only  $1.04 \pm 0.52$  kcal./mole.<sup>19</sup> The 3a and 8a hydrogens in compound 16 are *cis* to each other. No attempt was made to clarify the configuration of the C-8-methyl group.

(19) C. C. Browne and F. D. Rossini, *J. Phys. Chem.*, **64**, 927 (1960).

**III. The Catalytic Character of *n*-Butyllithium, Sodium, Potassium, and Cesium.**—*n*-Butyllithium was inert as a catalyst for the reactions of 6-phenyl-1-hexene and 7-phenyl-1-heptene; sodium caused isomerization of the double bond; potassium and cesium gave mostly cyclization products. The differences in catalytic behavior between *n*-butyllithium and sodium and potassium are enormous, while that between potassium and cesium is rather minor.

From the amounts of the tricyclic compounds formed during the reactions, cesium distinguished itself from potassium by favoring the "double cyclization." From the reaction of 6-phenyl-1-hexene, only cesium

	K	Cs
Compound 6/(4 + 5 + 6)	15.6%	27.9%
Compound 14/(12 + 13 + 14)	8.0%	11.1%

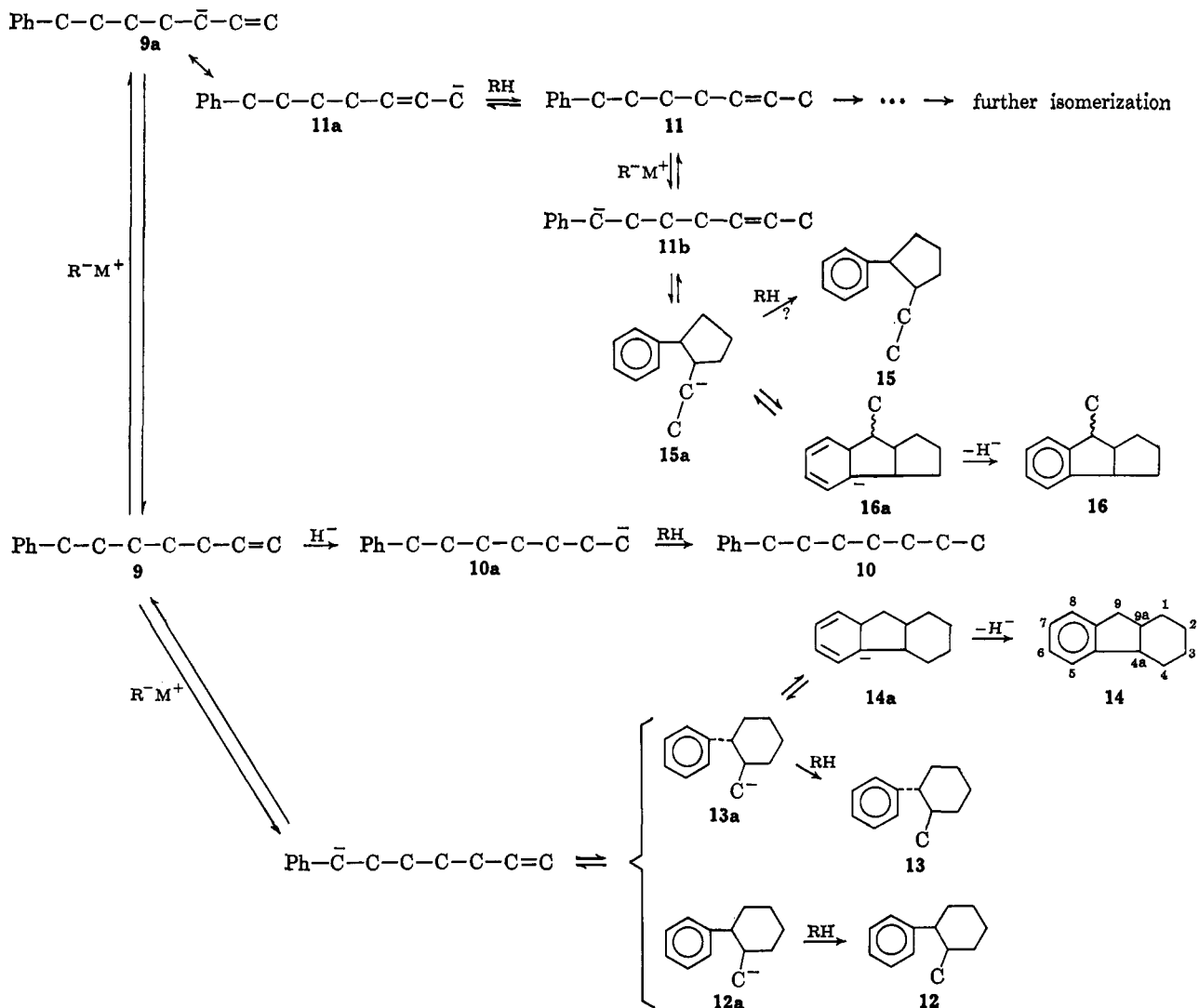
gave some phenylcyclohexane. However no phenylcycloheptane was detected from the reaction of 7-phenyl-1-heptene, even with cesium catalyst, owing to the fact that a seven-membered ring compound is generally not so readily formed as six-membered ones.

This finding, at least partly, can be related to the ionic character of the bond between carbon and the alkali metal (ionic character: C-Li 43%, C-Na 47%, C-K 52%, C-Cs 57%).<sup>20</sup> A more ionic species

(20) 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.

## SCHEME II

THE MECHANISM FOR THE FORMATION OF THE PRODUCTS FROM THE REACTION OF 7-PHENYL-1-HEPTENE

M<sup>+</sup> = alkali metal cationR<sup>-</sup> = C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub><sup>-</sup> (from the initiator) or any anion produced in the reaction

is probably more dissociated. In turn, its carbanions are electrostatically less stabilized by its cations. These carbanions from the more dissociated organoalkali metal compounds will show a higher reactivity as a consequence.

**IV. Intramolecular Alkylation (Cyclization) vs. Intermolecular Alkylation.**—The intermolecular alkylation of either 6-phenyl-1-hexene or 7-phenyl-1-heptene appeared to be absent in their reactions, although no direct attempt was made in order to verify it. In supplementary experiments, 6-phenyl-1-hexene under simulating conditions was found to be incapable of alkylation by either toluene or ethylbenzene. The absence of the intermolecular alkylation can be attributed to at least two factors. Both the intermolecular and intramolecular alkylations are accompanied by a negative entropy of activation owing to the decrease in the total number of molecules in one case and the special requirement of molecular orientation in another. Even though there are no definite data to justify their magnitudes, kinetically unimolecular transformations always have the advantage over bimolecular collisions. On the other hand, an alkylation reaction is undoubtedly subjected to steric effects especially

arising from the olefin used. The amount of the steric effect from the olefins can be roughly judged from the alkylation temperature required<sup>21</sup>: for ethylene, about 220°; propylene and 1-butene, about 290°; and isobutylene, about 350°. Therefore, at a reaction temperature of 185°, the intermolecular alkylation probably is insignificant, since  $\omega$ -phenyl-1-alkenes will be expected to behave like 1-butene sterically.

## Experimental

**Analytical Procedure.**—The reaction products were analyzed by means of vapor phase chromatography (v.p.c.). Part of the products was selectively hydrogenated at atmospheric pressure and temperature over palladium-on-charcoal or platinum oxide catalyst to reduce the olefinic groups. The hydrogenated products were distilled and the individual hydrocarbons were further separated in pure form by a preparative v.p.c. column. The structures of the various hydrocarbons were determined from their infrared, ultraviolet, and/or n.m.r. spectra<sup>22</sup> which

(21) H. Pines and V. Mark, *J. Am. Chem. Soc.*, **78**, 4316 (1956).

(22) The infrared spectra of pure liquid samples were taken in a 0.026-mm. sodium chloride cell with either a Baird Model AB-2 or Model 4-55. The ultraviolet spectra were determined in isooctane with a Beckman DK-2. The n.m.r. spectra were measured in carbon tetrachloride, using tetramethylsilane as an internal standard, with a Varian A-60.

were further compared with those of known compounds. In cases where the amount of the separated products was too small for spectral analysis, they were identified by v.p.c. over at least two different columns. The v.p.c. columns used are described in Table IV, and the relative retention times of the various hydrocarbons are given in Table V.

TABLE IV  
VAPOR PHASE CHROMATOGRAPHIC COLUMNS USED FOR  
ANALYSES AND SEPARATIONS

Column	Liquid phase (wt. %)	Chromosorb P, mesh	Column	Column o.d., in.
			length, m.	
A	Carbowax 20M (15)	35-60	2.0	0.25
B	Silicone oil DC-550 (8)	30-60	4.0	0.25
C	Silicone gum rubber SE-30 (30)	45-60	5.1	0.375
D	Carbowax 20M (15)	45-60	3.0	0.375
E	QF-1 (18)	45-60	5.0	0.25

TABLE V  
RELATIVE RETENTION TIMES OF THE HYDROCARBONS

Compd.	Column				
	A		B		E
	Temp., °C.				
	100	150	200	150	225
	Flow rate, ml./min.				
	82	75	75	75	75
Toluene	0.109				
<i>n</i> -Pentylbenzene	1.00		1.00		1.00
<i>n</i> -Hexylbenzene (2)		1.53		1.69	
<i>trans</i> -1-Methyl-2-phenylcyclopentane (4, 22)			1.82		1.74
6-Phenyl-1-hexene (1)			1.92		1.70
<i>cis</i> -1-Methyl-2-phenylcyclopentane (5, 23)			2.31		2.16
<i>n</i> -Heptylbenzene (10)			2.36		2.76
<i>trans</i> -1-Methyl-2-phenylcyclohexane (12, 32)			2.67	2.67	1.43
7-Phenyl-1-heptene (9)			2.91		2.78
Phenylcyclohexane (7)			0.802		
1,2,3,3a,8,8a-Hexahydrocyclopent[a]indene (6, 29)			3.46	0.922	2.86
<i>cis</i> -1-Methyl-2-phenylcyclohexane (13, 33)			3.94		3.91
Naphthalene			3.97	1.00	1.00
8-Methyl-1,2,3,3a,8,8a-hexahydrocyclopent[a]indene (16, 35)			4.79	1.22	4.15
1,2,3,4,4a,9a-Hexahydrofluorene (14, 36)			5.38	1.36	4.54
Phenylcycloheptane (17)				1.36	2.26
Biphenyl (8)				1.98	4.41

**Apparatus.**—The apparatus consisted of a three-necked round-bottom flask containing a thermocouple well. The flask was provided with a specially designed high-speed stirrer,<sup>23</sup> a Y-shaped adapter equipped with a reflux condenser and a dropping funnel, and a self-sealing rubber diaphragm through which samples were removed during the run by means of a syringe. Provision was made to collect gaseous products by passing them through a trap cooled by liquid nitrogen.

**Catalyst.**—*n*-Butyllithium (15% in hexane, Foote Mineral Co.) was mixed with *sec*-butylcyclohexane. Then hexane was removed by distillation. No initiator was used in the lithium-catalyzed reaction.

**Sodium and potassium** used in the reactions were freshly cut metals.

**Cesium** was transferred in its molten metallic form to a reaction flask which had repeatedly been evacuated and filled with helium gas.

**General Procedure (Table I).**—In a reaction flask was placed a mixture consisting of an inert solvent, *o*-chlorotoluene, and a catalyst. Under a helium atmosphere, the mixture was heated to refluxing and then stirred at high speed. At the end of 2 hr., the catalyst was obtained in a finely dispersed form.

$\omega$ -Phenyl-1-alkene was then added over a period of 1 hr. through a dropping funnel into the flask. The extent of the

reaction was followed by v.p.c. analysis. The per cent yield of each product was calculated by taking the inert solvent as an internal standard.

After the major reaction was over, the mixture was cooled, decomposed with isobutyl alcohol, washed with water until neutral, and finally dried over anhydrous calcium chloride. Then the reaction mixture was ready for further identification (see Analytical Procedure above).

**Reaction Products. A. From 6-Phenyl-1-hexene (Table II).**—Liquid products were separated by v.p.c., using columns C and D. *n*-Hexylbenzene (2, hydrogenated compound 3 and its isomers), *trans*- and *cis*-1-methyl-2-phenylcyclopentane (4,  $n^{20D}$  1.5162, and 5,  $n^{20D}$  1.5246) and 1,2,3,3a,8,8a-hexahydrocyclopent[a]indene [6,  $n^{21D}$  1.5505,  $\lambda_{max}$  273 m $\mu$  ( $\epsilon$  296)] were identified by their infrared spectra. The n.m.r. spectrum<sup>24</sup> of compound 4 had a phenyl H singlet ( $\delta$  6.93, area 5.0) and a methyl H doublet [ $\delta$  (center) 0.90, area 3.2]. The presence of phenylcyclohexane (7) and biphenyl (8) was confirmed by v.p.c. using columns A and B.

No essential amount of gases was produced during the reaction.

**B. From 7-Phenyl-1-heptene (Table III).**—The reaction products were separated by v.p.c. over column D. *n*-Heptylbenzene (10, hydrogenated compound 11 and its isomers) and *trans*- and *cis*-1-methyl-2-phenylcyclohexane (12,  $n^{20D}$  1.5170; 13,  $n^{20D}$  1.5277) were identified by their infrared spectra. Compounds 12 and 13 had methyl-H doublets at  $\delta$  (center) 0.69 and 0.66, respectively, in their n.m.r. spectra.<sup>24</sup> 1,2,3,4,4a,9a-Hexahydrofluorene (14) and 8-methyl-1,2,3,3a,8,8a-hexahydrocyclopent[a]indene (16) were characterized by their relative retention times in v.p.c. analyses over columns A and B. Phenylcycloheptane (17) was absent.

Only a trace of gas was generated from the reaction.

**Synthesis of Phenylalkenes and of Hydrocarbons Used for Identification.** 1.—6-Phenyl-1-hexene (1) was synthesized in 64% yield and 99.0% purity from 3-phenylpropylmagnesium bromide and allyl bromide. The title compound (1) was distilled at 100–102° (15 mm.):  $n^{25D}$  1.5008; lit.<sup>25</sup> b.p. 119° (30 mm.),  $n^{25D}$  1.5010.

2. 7-Phenyl-1-heptene (9). A.—4-Phenyl-1-butanol (18), b.p. 145–148° (17 mm.),  $n^{24D}$  1.5261, lit.<sup>26</sup> b.p. 135–140° (14 mm.), was obtained in 35% yield from 51 g. (2.1 g.-atoms) of magnesium, 370 g. (2.0 moles) of  $\beta$ -bromoethylbenzene, and 109 ml. (2.2 moles) of ethylene oxide by using a procedure similar to that of Dreger.<sup>27</sup>

B.—4-Phenylbutyl bromide (19) was obtained in 62% yield (b.p. 133–140° at 17 mm.,  $n^{27D}$  1.5373) by treating 90 g. (0.66 mole) of compound 18 with 179 g. (0.66 mole) of phosphorus tribromide, according to a procedure similar to that of Noller and Dinsmore.<sup>28</sup>

C.—7-Phenyl-1-heptene (9) was synthesized by a condensation reaction between 4-phenylbutylmagnesium bromide and allyl bromide and was obtained in 65% yield and 99.5% purity: b.p. 123–126° (26–28 mm.),  $n^{25D}$  1.4980 (lit.<sup>25</sup> b.p. 123° at 24 mm.,  $n^{22D}$  1.5007).

3. *trans*- and *cis*-1-Methyl-2-phenylcyclopentane (22, 23).—By treating phenylmagnesium bromide with 2-methylcyclopentanone, a crude mixture of *cis*- and *trans*-1-methyl-2-phenylcyclopentanol (20) was obtained in 56% yield. The alcohols (20) were then dehydrated either by phosphorus oxychloride-pyridine<sup>15</sup> or by potassium bisulfate to 1-methyl-2-phenylcyclopentenes (21), b.p. 103–111° (12 mm.). Subsequent catalytic hydrogenation over platinum oxide gave a mixture of *trans*- and *cis*-1-methyl-2-phenylcyclopentane (22, 23). The mixture obtained from the phosphorus oxychloride-pyridine dehydration procedure had a *cis/trans* (23/22) ratio of 2.8, while that from the potassium bisulfate procedure had a *cis/trans* ratio of 7.7.

Anal. Calcd. for C<sub>12</sub>H<sub>16</sub>: C, 89.94; H, 10.07. Found: C, 89.69; H, 10.06.

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4. **1,2,3,3a,8,8a-Hexahydrocyclopent[a]indene (29).** A.—Cyclopentene-1-carboxylic acid (26) was synthesized according to the procedure of Maitte.<sup>29</sup> 1,2-Dibromocyclopentane (24; 120 g., 0.53 mole) was dehydrobrominated at 120° (46 mm.) by a mixture of 170 g. of dry sand and 125 g. (2.2 moles) of powdered potassium hydroxide. 1-Bromocyclopentene (25) was obtained in 50% yield, b.p. 115–132°.

The Grignard reagent obtained when the bromide 25 (21 g., 0.15 mole) was treated with 4.8 g. (0.20 g.-atom) of magnesium in 50 ml. of purified tetrahydrofuran was carboxylated by Hussey's procedure.<sup>30</sup> The title compound (26) was obtained in 43% yield. After sublimation, it melted at 119–120° (lit.<sup>29</sup> m.p. 123–123.5°).

B.—1,2,3,3a,8,8a-Hexahydrocyclopent[a]indene (29) was synthesized after Baker and Jones.<sup>31</sup> The carboxylic acid 26 (8.8 g., 0.08 mole) was first converted with 10 ml. (0.14 mole) of thionyl chloride at 110° for 0.5 hr. to its acyl chloride (27, b.p. 72–73° at 19 mm.) with a yield of 85%. The acyl chloride (27; 8.7 g., 0.07 mole) was allowed to react with 75 ml. of benzene with constant stirring in the presence of 26.5 g. (0.20 mole) of aluminum chloride. The mixture was kept at 0° for 1 hr., then heated up to 110° for 2 hr., and allowed to stand overnight at room temperature. After decomposition of the mixture by dilute hydrochloric acid, the organic layer was washed and dried. An 86% yield of [2,3]cyclopenta-1-indanone (28) was obtained. On Clemmensen reduction,<sup>32</sup> 28 gave a 76% yield of the title compound (29) which was distilled at 120–122° (17 mm.),  $n_D^{20}$  1.5503 (lit.<sup>31</sup>  $n_D^{17}$  1.5511).

Anal. Calcd. for  $C_{12}H_{14}$ : C, 91.07; H, 8.91. Found: C, 90.75; H, 9.11.

5. **trans- and cis-1-Methyl-2-phenylcyclohexane (32, 33).**—The 1-phenyl-2-methylcyclohexanols (30), obtained from phenylmagnesium bromide and 2-methylcyclohexanone, b.p. 132–

139° (15 mm.), were dehydrated to 1-phenyl-2-methylcyclohexenes (31) by refluxing with a small amount of potassium bisulfate. Hydrogenation of the olefins over platinum oxide yielded a mixture of the title hydrocarbons (32, 33),  $n_D^{20}$  1.5258 (lit.<sup>33</sup>  $n_D^{18}$  1.5360). The ratio of *cis/trans* (33/32) isomers produced was 7.3.

Anal. Calcd. for  $C_{13}H_{18}$ : C, 89.60; H, 10.41. Found: C, 89.77; H, 10.29.

6. **8-Methyl-1,2,3,3a,8,8a-hexahydrocyclopent[a]indene (35).** A.—1-Methyl[2,3]cyclopenta-1-indanol (34) was prepared in 67% yield by treating 8.3 g. (0.059 mole) of methyl iodide, 1.4 g. (0.059 g.-atom) of magnesium, with 9.6 g. (0.056 mole) of [2,3]cyclopenta-1-indanone (28). Compound 34 recrystallized from *n*-hexane, m.p. 74–75°, and was characterized by an infrared absorption spectrum (KBr pellet)<sup>34</sup> having a band of methyl group at 7.29  $\mu$  and of hydroxyl group at 2.90  $\mu$ .

B. **8-Methyl-1,2,3,3a,8,8a-hexahydrocyclopent[a]indene (35).**—Dehydration of the alcohol 34 by means of a small amount of potassium bisulfate, followed by catalytic hydrogenation over platinum oxide, gave 1.5 g. of compound 35 in 37% yield: b.p. 120–124° (12 mm.),  $n_D^{15}$  1.5467.

Anal. Calcd. for  $C_{13}H_{18}$ : C, 90.64; H, 9.36. Found: C, 90.50; H, 9.41.

7. **1,2,3,4,4a,9a-Hexahydrofluorene (36).**—The hydrogenation of fluorene (47.5 g., 0.30 mole) was performed in a 450-ml. rotating autoclave in the presence of 4.0 g. of nickel-kieselguhr catalyst under an initial hydrogen pressure of 110 atm. at 150–170° for 4 hr. At the end of the reaction, the pressure had dropped to 56 atm. (at room temperature). Compound 36 was obtained in 64% yield: b.p. 124–125° (13 mm.),  $n_D^{20}$  1.5530 (lit.<sup>35</sup> b.p. 127° at 15 mm.,  $n_D^{10}$  1.5572).

Anal. Calcd. for  $C_{13}H_{18}$ : C, 90.64; H, 9.36. Found: C, 91.00; H, 9.24.

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## The Alkali Metal Catalyzed Reactions of $\omega$ -Phenyl-1-alkenes. The Dimerization of 4-Phenyl-1-butene. The Cleavage and Cyclization Reaction of 5-Phenyl-1-pentene<sup>1,2</sup>

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The reaction of 4-phenyl-1-butene and of 5-phenyl-1-pentene in the presence of sodium, potassium, and cesium has been studied. 4-Phenyl-1-butene at 185° in the presence of potassium as a catalyst yielded 39.6% of 1-phenyl-2-ethyl-3-benzylcyclopentane, 23.7% of butylbenzene, and some naphthalene. 5-Phenyl-1-pentene at 135° in the presence of potassium or cesium as a catalyst gave  $C_2$  and  $C_4$  gases, toluene, ethylbenzene, 1,3-diphenylpropane, 1-methylnaphthalene, phenylcyclopentane, etc. The difference in catalytic behavior between potassium and cesium was characterized by (1) production of cyclopropane and allene only in the potassium-catalyzed reaction, and (2) the ratio of cleavage products to cyclization products being greater with potassium than with cesium. Sodium caused primarily the migration of double bonds.

The alkali metal catalyzed reactions<sup>4,5</sup> of 6-phenyl-1-hexene and 7-phenyl-1-heptene have been described in the preceding papers.<sup>1,6</sup> In the presence of potassium or cesium as catalyst, the predominant reaction was the cyclization resulting in the formation of 1-methyl-2-phenylcyclopentane from 6-phenyl-1-hexene and of 1-

methyl-2-phenylcyclohexane from 7-phenyl-1-heptene. The size of the rings seemed to be determined by the stability of their carbanion intermediates (polar effect, *i.e.*, primary > secondary > tertiary). On the other hand, sodium as catalyst gave products<sup>5</sup> mainly resulting from double-bond migrations.

In order to shed more light on the possible merits and limitations of this type of reaction, these studies have been extended to 4-phenyl-1-butene and 5-phenyl-1-pentene. The primary purpose was to investigate whether these hydrocarbons might undergo cyclization reactions under the conditions described in the preceding papers.<sup>1,6</sup> The catalysts used in this study were sodium, potassium, and cesium.

(1) Paper XXX of the series, "Base-Catalyzed Reactions". Paper XXIX: H. Pines, N. C. Sih, and E. Lewicki, *J. Org. Chem.*, **30**, 1457 (1965).

(2) This work was supported in part by a National Science Foundation Grant, NSF-G14503.

(3) Taken in part from the Ph.D. Thesis of N. C. Sih, Northwestern University, June 1964.

(4) The actual catalyst is alkali metal-organoalkali metal.

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