Free-Radical-Induced Cyclization of ω-Phenyl-1-alkenes[1]

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The reactions of ω-phenyl-1-alkenes, PhC$_n$C=C (n = 2–5), in the presence of di-*t*-butyl peroxide have been studied at 140–150°. The monomeric products obtained in 24% yield from 6-phenyl-1-hexene consisted mainly of *cis*- and *trans*-1-methyl-2-phenylcyclopentane. Smaller amounts of phenylcyclohexane and of a tricyclic hydrocarbon, 1,2,3,3a,8,8a-hexahydrocyclopent[*a*]indene, were also produced. Under similar experimental conditions, 7-phenyl-1-heptene yielded, besides *cis*- and *trans*-1-methyl-2-phenylcyclohexane and 1,2,3,4,4a,9a-hexahydrofluorene, also *n*-octylbenzene resulting from the addition of a methyl radical to the phenylalkene. The total yield was 10.4%. 5-Phenyl-1-pentene formed 4.4% of monomeric products consisting of *n*-hexylbenzene and cyclopentylbenzene. 4-Phenyl-1-butene produced only 3.0% in *n*-pentylbenzene. The monomeric products from the reaction of 6-phenyl-1-hexene with benzoyl peroxide were similar to those obtained from di-*t*-butyl peroxide.

Recent studies in our laboratory have demonstrated that certain ω-phenyl-1-alkenes undergo intramolecular alkylation (cyclization) in the presence of potassium or cesium as catalyst.[3] The cyclic products were five- and six-membered ring compounds and were derived almost exclusively from the more stable primary carbanions as precursors. For example, 6-phenyl-1-hexene yielded 57% of *cis*- and *trans*-1-methyl-2-phenylcyclopentane and 11% of 1,2,3,3a,8,8a-hexahydrocyclopent[*a*]indene. On the other hand, 4-phenyl-1-butene dimerized and 5-phenyl-1-pentene underwent a fission reaction.[4] This investigation has been extended in order to determine the feasibility of intramolecular cyclization by free-radical-induced reactions. Di-*t*-butyl peroxide and benzoyl peroxide were used as radical initiators.

Results and Discussion

Di-*t*-butyl Peroxide (DBP).—The di-*t*-butyl peroxide induced reactions of ω-phenyl-1-alkenes proceeded readily at 140–150°, and about 80% of the monomeric compounds was produced within the first hour of the reaction. The initiation occurred through the decomposition of the peroxide with the formation of *t*-butoxy and of methyl radicals.[5]

The reaction product was composed of "monomeric" and "polymeric" materials, and only the former were investigated (Tables I and II). There were two major reactions leading to the monomeric products: (1) methyl addition to the terminal double bond of olefins, Ph-C$_n$-C=C (n = 2, 3, and 5), which eventually resulted in the formation of *n*-alkylbenzenes (see Scheme I), and (2) intramolecular cyclization of olefins (n = 3, 4, and 5), forming compounds having general formulas III (n = 4 and 5), IV (n = 4 and 5), and VII (n = 3, 4, and 5) (see Scheme I).

The methyl addition to the olefins occurred only at the terminal vinylic carbon *via* a secondary radical intermediate, which is in accord with the concept of the relative stability of the free radicals, namely tertiary > secondary > primary.

The cyclization reaction took place through the formation of benzylic radicals produced by the removal of a hydrogen atom from phenylalkenes by methyl or *t*-butoxy radicals. The interesting feature of this reaction is that a stable secondary benzylic radical adds intramolecularly to a terminal double bond to form preferentially the least-stable resonance nonstabilized primary radical. The products of the general formulas III and IV obtained from the primary radical intermediates surpassed substantially that of the general formula VII derived from the secondary radicals. It has been reported from a thermal alkylation study of toluene and propylene that the preference for the formation of a secondary free-radical intermediate over a primary one is about a factor of 4, even at a temperature of 430°.[6]

Similar type of cyclization involving primary free radicals and leading to the formation of methylcyclopentane was recently reported to occur during the decomposition of 6-heptenoyl peroxide[7] and from the reaction 6-mercapto-1-hexene with triethyl phosphites.[8] Similar cyclization was observed during the addition of perfluoropropyliodide to 1,6-heptadiene.[9]

Cyclization leading to compound VII could not have occurred with prior isomerization, since ω-phenyl-2-alkenes were not detected among the products of reaction. Furthermore, had such isomerization taken place, then 7-phenyl-2-heptene would have yielded 1-ethyl-2-phenylcyclopentane.

It is interesting to note that monomeric products obtained from the reaction of 6-phenyl-1-hexene with di-*t*-butyl peroxide did not contain *n*-heptylbenzene by methylation. Such methylation occurred, however, with all the other ω-phenylalkenes.

The secondary cyclization reactions resulting in the formation of 1,2,3,3a,8,8a-hexahydrocyclopent[*a*]-indene (**4**) from 6-phenyl-1-hexene and of 1,2,3,4,4a,9a-hexahydrogluorene (**11**) from 7-phenyl-1-heptene were also observed in the base-catalyzed reactions described previously by us.[3] Although the cyclization of simple olefins induced by radicals to form cyclopentane and cyclohexane derivatives has not been mentioned in the literature to our knowledge, this type of radical intermediates were used to explain the cycloparaffin formations in thermal dimerization of propylene and butenes.[10]

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TABLE I

THE COMPOSITION OF THE MONOMERIC PRODUCTS FROM THE PEROXIDE-INDUCED REACTION OF 6-PHENYL-1-HEXENE

Peroxide used, mole	DBP, 5.4×10^{-3}	BP, 5.0×10^{-3}	BP, 5.0×10^{-3}
Solvent used, ml	...	...	*n*-heptane (24)
Reaction temp, °C	140–150	90	85
Moles of 6-phenylhexene used	2.2×10^{-2}	2.0×10^{-2}	2.0×10^{-2}
6-Phenylhexene reacted, %	49.2	40.0	13.0
Total yield of the monomeric products, mole %	24[a,c]	5.0[b,d]	3.8[b,d]
trans-1-Methyl-2-phenylcyclopentane (**1**)	52	58	64
cis-1-Methyl-2-phenylcyclopentane (**2**)	32	19	10
Phenylcyclohexane (**3**)	8	9	7
1,2,3,3a,8,8a-Hexahydrocyclopent[*a*]indene	8	13	19
Ratio of compound **3**/(**1** + **2** + **4**)	1:8.7	1:10	1:7.5
Ratio of compound **4**/(**1** + **2**)	1:11	1:5.9	1:3.9

[a] Other products were methane (76 ml at STP), acetone, and *t*-butyl alcohol. [b] Other products were carbon dioxide (59 ml without solvent and 50 ml with solvent at STP), benzene, benzoic acid, biphenyl, and terphenyls(?). [c] Yield = moles of product/2 × (moles of peroxide consumed − moles of ethane formed). [d] Yield = moles of product/moles of peroxide used. The amount of biphenyl and possibly some terphenyls was not determined.

TABLE II

THE MONOMERIC PRODUCTS FROM THE DI-*t*-BUTYL PEROXIDE INDUCED REACTION OF ω-PHENYL-1-ALKENES AT 140–150°[a,b]

4-Phenyl-1-butene	
Total yield of the monomeric product, mole %[c]	3.0
n-Pentylbenzene (**5**)	~100
5-Phenyl-1-pentene	
Unreacted olefin recovered, mole %	45.3
Total yield of the monomeric products, mole %	4.4
Composition, mole %	
n-Hexylbenzene (**6**)	64
Cyclopentylbenzene (**7**)	14
Others	22
7-Phenyl-1-heptene	
Unreacted olefin recovered, mole %	
Total yield of the monomeric products, mole %[c]	10.4
Composition, mole %	
n-Octylbenzene (**8**)	34
trans-1-Methyl-2-phenylcyclohexane (**9**)	31
cis-1-Methyl-2-phenylcyclohexane (**10**)	18
1,2,3,4,4a,9a-Hexahydrofluorene (**11**)	17
Cycloheptylbenzene (**12**)	Trace

[a] Methane, acetone, and *t*-butyl alcohol were also produced from the reactions. Ethane was detected only from the reaction of 7-phenyl-1-heptene (ethane:methane = 1:10). The amount of methane was 75, 42, and 43 ml at STP for $PhC_nC{=}C$ when n = 2, 3, and 5, respectively. [b] Molar ratio of olefin:peroxide used = 4:1. [c] Same as footnote *c* in Table I.

A peroxide-induced cyclization reaction leading to an indanone was recently reported in a nonhydrocarbon system, *i.e.*, phenylalkylaldehyde.[11] With hydrocarbons, cyclization leading to indans was noticed in thermal alkylation of alkylbenzenes with olefins.[12]

Although there is close resemblance between the base-catalyzed reactions of ω-phenyl-1-alkenes and those induced by free radicals, there is enough evidence to point out that the two reactions occur by anionic and free radical mechanisms, respectively. The reaction of 6-phenyl-1-hexene in the presence of sodium and potassium produces on cyclization 1-phenyl-2-methylcyclopentane at the exclusion of phenylcyclohexane. This is in agreement with the selectivity encountered in the addition of toluene to propylene in the presence of sodiumorganosodium catalyst. Isobutylbenzene was the monoadduct formed, *n*-butylbenzene being absent, which indicates that the anionic addition to the double bond is governed by the relative stability of the intermediate anions, namely, tertiary > secondary > primary.[13] The yield of high boiling material obtained from the reaction of 6-phenyl-1-hexene with sodium and cesium was less than 1%. A high yield of dimeric material would be expected if the alkali metal catalyzed cyclization would proceed *via* a free-radical mechanism. The secondary benzylic free radical, if present, would most certainly undergo extensive dimerization reaction.

Benzoyl Peroxide (BP).—The same general trend as with di-*t*-butyl peroxide, was observed with the benzoyl peroxide induced reaction of 6-phenyl-1-hexene at 85–90°, except that the yield of the monomeric products was lower (Table I). The fact, that the phenyl radicals from benzoyl peroxide dimerized in the reaction medium more readily than methyl radicals from di-*t*-butyl peroxide made the former a less effective initiator. The solvent, *n*-heptane, seemed to suppress the formation of polymeric materials as indicated by the higher yield of the monomeric products relative to the olefin consumed.

Experimental Section

Materials.—The ω-phenylalkenes and compounds used for identification were synthesized according to the procedures described previously.[3,4]

Reaction Procedure.—The reactions were carried out in a microdistillation apparatus. The reaction flask was charged with olefin and the system preheated to the reaction temperature, then connected to a gas collecting bottle. Benzoyl peroxide was introduced into the flask in a solid form and di-*t*-butyl peroxide through a rubber diaphragm. The low-boiling decomposition products (from peroxide) were continuously distilled out into a receiver in order to maintain the reaction temperature constant in the flask. After the evolution of the gases ceased, the flask was cooled and 1,4-di-*t*-butylcyclohexane or naphthalene added as an internal quantitative standard for gas chromatographic analysis. A part of the reaction mixture was hydrogenated over 5% palladium on charcoal catalyst in order to determine the amount of *trans* compounds (**1** and **9**). The products were identified by gas chromatography (F & M, Model 720) and/or by infrared spectroscopy (Beckman A-5).

Chromatographic Analysis.—The gases were analyzed over a column of 0.25 in. × 2.4 m of Davison's 950 silica gel, other compounds by two columns: 0.25 in. × 2.0 m of 15% Carbowax 20M on 35–60 mesh Chromosorb P, and 0.25 in. × 4.0 m of 8% silicone oil DC-550 on 30–60 mesh Chromosorb P. The unreacted di-*t*-butyl peroxide (mostly in the distillate) was determined at column temperature of 50° and inject port tempera-

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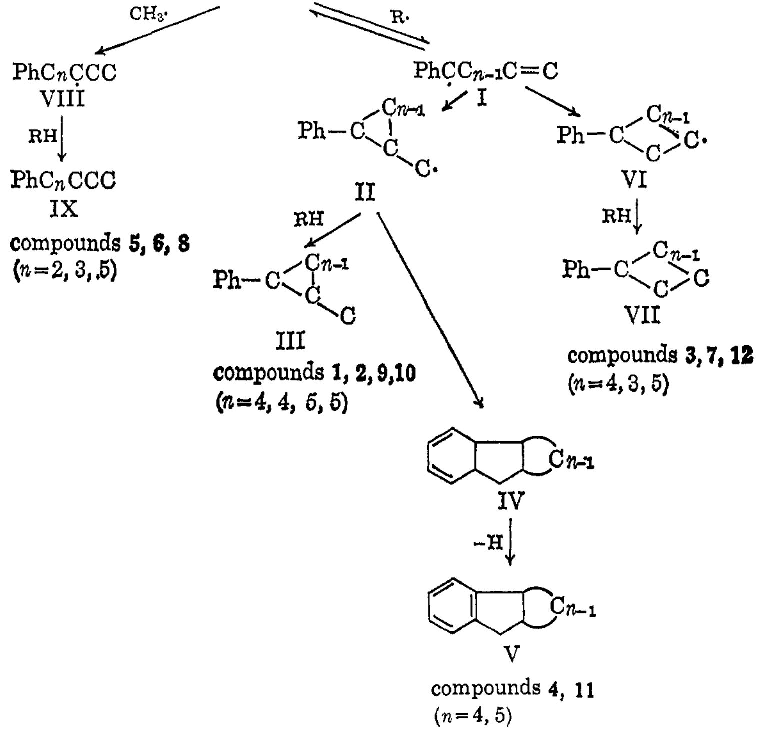
SCHEME I

FORMATION OF THE MONOMERIC PRODUCTS FROM ω-PHENYL-1-ALKENES



ture of 90°; otherwise decomposition would occur at higher temperatures. The molar area responses (over Carbowax 20M column) are as follows: (A) di-*t*-butyl peroxide, 1.0; *t*-butyl alcohol, 0.58; acetone, 0.44; (B) naphthalene, 1.0; 6-phenyl-1-hexene, 0.94: phenylcyclohexane, 0.71; 1,2,3,3a,8,8a-hexahydrocyclopent[*a*]indene, 0.78; 1-methyl-2-phenylcyclopentanes, 0.62; *n*-hexylbenzene, 1.0, and (C) 1,4-di-*t*-butylcyclohexane, 1.0; 1-methyl-2-phenylcyclohexane, 0.87; 1,2,3,4,4a,9a-hexahydrofluorene, 0.70; *n*-heptylbenzene, 0.91. Their relative retention times were tabulated in the preceding papers.[3,4]

Resin Acids. IX. Cationic Cyclization of Pimaric Acid Derivatives. Partial Synthesis of (−)-Hibaene[1]

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The partial synthesis of (−)-hibaene and (−)-hibane from pimaric acid is described. Cationic cyclization of methyl 16-hydroxy-$\Delta^{8(14)}$- and $\Delta^{8(9)}$-dihydropimarate alkyl and arylsulfonates did not result in derivatives of hibane, but led, contrary to expectations, to compounds of type **16** with rearrangement of the carbon skeleton.

The tetracyclic diterpene (−)-hibaene (**1**) (Chart I) has been isolated in two laboratories[3,4] from different sources and its structure elucidated.[3] Its enantiomer (+)-hibaene **2a** (stachene) has also been encountered in nature.[5,6] The absolute configuration assigned to these compounds has been confirmed by correlation[7] of monogynol **2b** with isostevane **3** and conversion[8] of (+)-hibaene to (−)-kaurene (**4**). More recently, the total synthesis of the racemate has been accomplished.[9]

Our own efforts in this area were begun before the discovery of the hibaenes and their derivatives[10] and were based on the notion that cationically induced cyclization of suitably substituted derivatives of pimaradienes **5** might lead to compounds based on the carbon skeleton **6** whose eventual discovery in nature could be anticipated. Choice of starting material was originally dictated by the relative accessibility of isopimaric acid **7**. In the event this led[11] to substances which turned out to be derivatives of isohibaene **8**

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