

The procedures listed in the Experimental Section for methylenation of 4 and 7 may be used as general guides for ketones and esters, respectively. One potential side reaction of ketones is the formation of $\text{Cp}_2\text{TiCH}_2\text{CR}_2\text{CH}_2$ (9) by the combination of the olefin produced and excess 1. These compounds serve as good methylenation agents when heated above their decomposition point⁶ and normally react with ketone present to form 2 equiv of olefin and $(\text{Cp}_2\text{Ti}=\text{O})$.⁷ If unquenched by ketone, 9 will be hydrolyzed upon workup to give the *gem*-dimethyl product 10.⁸ Therefore, use of a slight excess of ketone or warming the reaction above $\sim 60^\circ\text{C}$ before quenching is advised. Conversely, metallacycle formation with vinyl ethers has never been observed and should present no problem in reacting in situ 1 with esters. Potential side reactions of carbonyl starting materials and methylenation products with organoaluminum species present during these reactions does not appear to proceed to a significant degree.

Experimental Section

General Procedures. ^1H and ^{13}C NMR spectra were recorded on a JEOL FX-90Q (89.60 MHz ^1H , 22.53 MHz ^{13}C). Chemical shifts are referenced to residual protiosolvent residues. Elemental analysis was performed by L. Henling at the analytical facilities of the California Institute of Technology.

Materials. Titanocene dichloride (Boulder) was purified by Soxhlet extraction with CH_2Cl_2 before use. AlMe_3 (2.0 M in PhMe) was purchased from Aldrich (packaged under nitrogen in Sure/Seal bottles). 2-*tert*-Butylcyclohexanone (2), 4-phenylcyclohexanone (4), and dihydrocoumarin (7) were also purchased from Aldrich and used as received. Dry THF was previously distilled from sodium benzophenone ketyl and stored in solvent flasks equipped with Teflon screw-type valves. Solvents listed as reagent or technical were used as received. Silica gel (60, 230-400 mesh ATM) was purchased from EM reagents.

"Titration" of in Situ Solutions of 1. Solutions of 1 were prepared as below by using titanocene dichloride (2.49 g, 10.0 mmol) and AlMe_3 (2.0 M in PhMe, 10 mL, 20.0 mmol of AlMe_3). After the solution was stirred as described in Table I, 2-*tert*-butylcyclohexanone (2) (1.54 g, 10.0 mmol) in 30 mL of THF was treated with the prepared solution of 1 as below with stirring continued 0.5 h at -40°C and an additional 15 min at room temperature. Workup as below gave quantitative crude yields of organic products as a mixture of ketone and olefin. ^1H NMR integration of the *tert*-butyl resonances of 2 and 3 were used to calculate equivalents of 1 produced.

Preparation of (4-Methylenecyclohex-1-yl)benzene (5). A three-neck 250-mL round-bottom flask equipped with a magnetic stir bar and oil bubbler was charged with titanocene dichloride (12.45 g, 50.0 mmol) and flushed with argon, and AlMe_3 (2.0 M in PhMe, 55 mL total, 110 mmol of AlMe_3) was added by cannula from a graduated cylinder (the graduated cylinder was previously flushed with argon, capped with a rubber septum and charged by cannula from an Aldrich Sure/Seal bottle). The resulting dark red mixture was stirred at room temperature with initial evolution of CH_4 through the bubbler. After 72 h of stirring, additional AlMe_3 (2.0 M in PhMe, 20 mL total, 40 mmol of AlMe_3) was added by the above method and stirring continued for 12 h.

A 500-mL round-bottom flask equipped with magnetic stir bar and charged with 4-phenylcyclohexanone (4) (11.32 g, 65.0 mmol) was flushed with argon and capped with a rubber septum. A 80-mL sample of dry THF was added by syringe and the resulting solution stirred and cooled to -40°C . The previously prepared solution of 1 was added via cannula over a 10-min period while the resulting mixture was maintained at or below -40°C . Stirring was continued for 0.5 h at -40°C , 1.5 h at -40 to 0°C , and finally 1 h at room temperature.

The resulting dark red mixture was diluted with 50 mL of reagent THF added by syringe, vigorously stirred, and cooled to -10°C . A 40-mL sample of 15% NaOH (aqueous) was added initially in 0.2-0.3-mL portions by syringe with vigorous evolution of CH_4 , while the mixture was maintained at -10°C or below. When the mixture became too viscous for magnetic stirring, the flask was swirled by hand with frequent cooling and the remainder of the NaOH solution was added in much larger portions to the open flask. Additional stirring at room temperature produced a mixture containing a pale orange supernatant with a large amount of slightly bluish precipitate which turned white upon standing. The aluminosilicate polymer formed serves as an excellent drying agent, and no further drying was required.

The mixture was filtered through a Celite pad on a coarse frit with suction and the precipitate and pad liberally washed with technical Et_2O . The combined filtrate and washings were evaporated under reduced pressure to afford a clear orange toluene solution of crude product which was diluted with 300 mL of reagent pentane to precipitate a large amount of orange solid. After filtration through a silica gel pad (on a coarse frit with suction) with liberally washing of the precipitate with reagent pentane, the combined washing and filtrate were evaporated under reduced pressure to give 10.57 g (94% yield) of product as a yellow oil. Vacuum distillation (bp 88°C (2 torr)) afforded 9.21 g (82% yield) of pure 5 as a colorless oil: ^1H NMR (CD_2Cl_2) δ 7.26 (m, 5 H), 4.72 (m, 2 H), 2.89-1.45 (m, 9 H); ^{13}C NMR (CD_2Cl_2) δ 149.4, 147.5, 128.8, 127.3, 126.4, 107.6, 44.6, 36.1, 35.7. Anal. Calcd for $\text{C}_{13}\text{H}_{16}$: C, 90.64; H, 9.36. Found: C, 90.66; H, 9.50.

Preparation of 3,4-Dihydro-2-methylene-2H-1-benzopyran (8). Dihydrocoumarin (7) (7.41 g, 50.0 mmol) was treated as above to give a toluene solution of crude 8. Due to the insolubility of 8 in pentane, an alternative method of purification was employed. This consisted of evaporation of the toluene under reduced pressure at 50°C to give a deep orange oil containing significant quantities of titanocene compounds (^1H NMR), followed by vacuum distillation to afford 5.56 g (76% yield) of 8^{1b} as a slightly yellow oil: ^1H NMR (CD_2Cl_2) δ 7.04 (m, 4 H), 4.54 (s, 1 H), 4.17 (m, 1 H), 2.74 (m, 2 H), 2.64 (m, 2 H); ^{13}C NMR (CD_2Cl_2) δ 156.8, 153.6, 129.2, 128.1, 123.5, 121.6, 116.3, 89.5, 27.0, 25.7. Anal. Calcd for $\text{C}_{10}\text{H}_{10}\text{O}$: C, 82.16; H, 6.89. Found: C, 81.77; H, 6.98.

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Registry No. 1, 67719-69-1; 2, 1728-46-7; 3, 1728-46-7; 4, 4894-75-1; 5, 87143-17-7; 6, 77933-59-6; 7, 119-84-6; 8, 74104-13-5; Cp_2TiCl_2 , 1271-19-8; $\text{Cp}_2\text{Ti}=\text{O}$, 59487-89-7; Cp_2TiMeCl , 1278-83-7; AlMe_3 , 75-24-1; AlMe_2Cl , 1184-58-3.

Liquid-Phase Radical Reactions of Octanal and *tert*-Butyl Hydroperoxide

George W. Mushrush* and Robert N. Hazlett

Chemistry Division, Combustion and Fuels Branch,
Code 6180, Naval Research Laboratory,
Washington, D.C. 20375-5000

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Introduction

The reaction of alkyl hydroperoxides with aldehydes has received little attention in the literature despite the practical significance this process holds in the autoxidation of such diverse materials as edible oils and distillate fuels.¹⁻⁵ Much of what has been reported is characterized

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Table I. Mole Percent Conversion for the Reaction of Octanal with *tert*-Butyl Hydroperoxide in Benzene Solvent at 140 °C

product	conversion (mol %)				
	15 ^a	30 ^a	60 ^a	120 ^a	180 ^a
<i>tert</i> -butyl hydroperoxide derived					
acetone	1.3	2.1	3.3	4.6	6.1
<i>tert</i> -butyl alcohol	30.0	41.7	56.7	65.5	69.3
di- <i>tert</i> -butyl peroxide	0.1	0.1	0.3	0.2	0.2
octanal derived					
heptane	27.9	46.2	48.4	55.1	54.6
heptene	0.1	0.2	0.2	0.2	0.2
hexane	0.1	0.4	0.6	1.0	1.2
<i>n</i> -heptanol	0.2	0.2	0.5	0.5	0.6
<i>n</i> -octanol	0.2	0.2	0.1		
heptanoic acid		0.1	0.1	0.1	0.1
octanoic acid	30.5	28.7	27.4	27.4	27.1
condensation products					
methyl octanoate	0.1	0.1	0.2	0.2	0.1
<i>tert</i> -butyl octanoate	0.1	0.1	0.2	0.2	0.1
heptyl <i>tert</i> -butyl ether	0.4	0.7	0.8	0.9	0.5
heptyl <i>tert</i> -butyl peroxide	1.0	1.5	1.3	0.8	0.4
solvent derived					
toluene	0.1	0.1	0.1	0.2	0.3
<i>n</i> -heptylbenzene	0.3	0.5	0.7	1.0	1.0
gaseous products					
carbon monoxide	28.1	47.1	51.0	55.4	56.8
methane	1.0	1.5	2.3	3.0	3.8
isobutylene	13.0	12.2	10.9	9.7	9.2
carbon dioxide	1.0	1.1	1.3	1.3	1.5
unreacted (reactants)					
<i>tert</i> -butyl hydroperoxide	51.1	36.4	25.7	14.3	8.9
octanal	26.6	11.5	4.0	2.5	0.7

^a Reaction time in minutes.

by experimental conditions which are difficult to reproduce and analytical methods which fail to account for many of the major reaction products which are formed.

The thermal decomposition of alkyl hydroperoxides, unlike that of dialkyl peroxides, is complex.^{6,7} At temperatures greater than 120 °C, *tert*-butyl hydroperoxide (*t*-BHP) decomposes by an autoinitiated pathway.⁸ The major reaction pathway in the 140 °C decomposition of *t*-BHP involves its attack by free radicals in the solution. The detailed mechanism of *t*-BHP decomposition is complicated since radical behavior is sensitive to structural, solvent, and stereoelectronic effects.

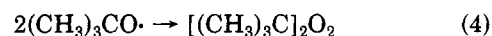
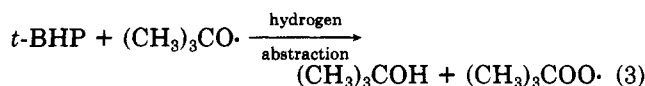
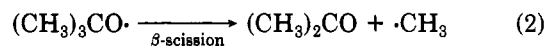
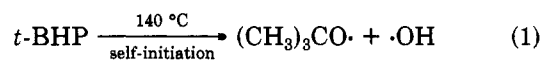
In an effort to clarify this situation, we have examined the reaction between *t*-BHP and octanal in dilute concentration in deaerated benzene solvent at 140 °C for time periods of 15–180 min. The time periods and the reaction temperature were selected such that the product mix could be studied from the initial concentration of both reactants to a time period (180 min) when both reactants were present in low concentration. The results indicate that although radical oxidation kinetics are expected to be complex, it is possible to explain the distribution of the major products in terms of a few competing reactions. Furthermore, we have developed reaction conditions and an analytical method of high reproducibility which may be applicable to the study of other *t*-BHP oxidative processes.

Results and Discussion

The results in Table I illustrate that the product distribution from the reaction of octanal with *t*-BHP in deaerated benzene solvent can be conveniently divided into

lower and higher molecular products. The quantities in the table are based on per cent conversion from the moles of reactants originally present. Products derived solely from octanal are calculated on the basis of starting amount of octanal. The *t*-BHP derived products (for example, *tert*-butyl alcohol) are similarly calculated based on the starting amount of *t*-BHP. Mixed condensation products (i.e., *t*-BHP + octanal) are calculated on the basis of moles of octanal. From octanal, major products were heptane, octanoic acid, and carbon monoxide; minor products were alcohols, ketones, alkenes, and shorter chain alkanes. From *t*-BHP, major products were acetone and *tert*-butyl alcohol; minor products were methane and di-*tert*-butyl peroxide. Condensation products included esters of octanoic acid, heptyl *tert*-butyl peroxide and heptyl *tert*-butyl ether. Solvent participation was indicated by the formation of toluene and *n*-heptyl benzene.

***t*-BHP Products.** The overall decomposition of *t*-BHP can be portrayed as shown in eq 1–4.



In aliphatic hydrocarbon solvent at temperatures of 100 °C or less, β -scission of the *tert*-butoxy radical is favored over hydrogen abstraction.⁹ In the aromatic solvent of this study, β -scission was found to be less important than hydrogen abstraction. This was confirmed by a comparison of the yields of acetone (1.3% at 15 min to 6.1% at 180 min) to the yield of *tert*-butyl alcohol (30.0% at 15 min

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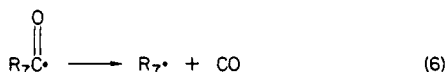
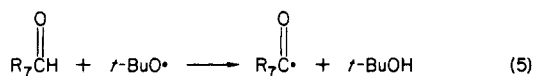
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increasing to 69.3% at 180 min). The termination product di-*tert*-butyl peroxide (0.1%) was present in low yield at all reaction periods.

Of the radicals generated by the processes depicted in steps 1-3, the *tert*-butylperoxy radical (step 3) was probably the least reactive. Thus, it would be expected to selectively form termination products. The heptyl *tert*-butyl peroxide resulted from such a process. Products that appear to be formed by termination steps involving other radicals such as the alkoxy radical (i.e., heptyl *tert*-butyl ether) were most likely formed as a result of an S_H2 type reaction.

Octanal Products. The major lower molecular weight products from octanal oxidation was heptane. Its yield varied from 27.9% at 15 min to 54.6% at 180 min of reaction. Other products included heptene (0.1-0.2%), hexane (0.1-1.2%), octanol (0.2-0.1%), and heptanol (0.2-0.6%). Minor (less than 0.1%) products observed were pentyloxirane, isomeric heptanols, and branched tetradecanes.

Heptane, the major alkane product, forms via hydrogen abstraction and subsequent decarbonylation of the acyl radical. The lower energy required for hydrogen abstraction from an aldehyde compared to a paraffin makes the aldehyde a favored reactant with both the alkoxy and the peroxy radicals generated in the system. The acyl radical once produced decarbonylates readily (steps 5 and 6).



Unsubstituted aliphatic aldehydes give the highest yield of acyl radicals.¹⁰

The acyl and heptyl radicals once produced can react by several paths to yield molecular products. The heptyl radical produces heptane by hydrogen abstraction. The hydrogen abstraction could be from any of several molecules. For example



this reaction would yield the *tert*-butylperoxy radical. Another attractive pathway would be the reaction with the starting aldehyde to yield heptane and an acyl radical or by disproportionation to yield heptene. Heptene could also be formed by hydrogen abstraction from the heptyl radical by a *tert*-butylperoxy radical. The low yield of heptene (0.1-0.2%) indicates these latter paths were not important reactions. The heptyl radical can also undergo termination reactions with several other radical in the system. Reaction with the hydroxyl radical afforded alcohols. However, alcohols could also be the result of an S_H2 type reaction with *tert*-BHP. Reaction with the methyl radical yielded *n*-octane and isomeric branched methyl heptanes. The C₈ hydrocarbons were minor (less than 0.1%) at all reaction times.

Gaseous Products. The gaseous products formed included carbon monoxide, isobutylene, methane, and carbon dioxide. Trace, but detectable, amounts of ethane and propane were also formed. No free oxygen was observed in any of the runs. As indicated in the table, CO increased from 28.1% to 56.8% at 180 min. Isobutylene was 13.0% initially and decreased to 9.2% at 180 min. Carbon dioxide

was uniformly low increasing slightly to 1.5% at 180 min. Methane increased from 1.0% at 15 min to 3.8% at 180 min of reaction.

Carbon monoxide was the major gaseous product formed. Its yield closely mirrored the yield of alkanes generated in the product mix. The heptyl radical once formed has, as indicated, many viable reaction paths. Consequently, the heptane yield was always a little less than the carbon monoxide yield.

The other major low molecular weight product was isobutylene. This product probably resulted from the acid-catalyzed dehydration of *tert*-butyl alcohol.¹¹ The decreasing isobutylene yield (13.0-9.2% at 180 min) was not surprising in light of the many pathways open to a reactive olefin in a radical environment.

The methane yield was similar to that of acetone. This was expected since they both form via β-scission of the alkoxy radical (reaction b). The reactive methyl radical easily abstracts hydrogen to yield methane rather than reacting with other radicals present in the system. This accounts for the low yield of branched hydrocarbons and other methyl radical derived products.

Carbon dioxide was the other gaseous product. Several mechanisms could account for its formation, but the most probable was a decarboxylation of the octanoic acid. This would account for the observed decrease of the acid as reaction time increased.

No free oxygen was observed at any reaction time. The lack of measured oxygen does not mean that it was not formed. It could form from a nonterminating reaction between two *tert*-butylperoxy radicals and then be consumed immediately by any of several pathways. Among these are the following: a reaction with CO, or more likely, a reaction with an acyl radical to ultimately generate octanoic acid since the peracid is an intermediate.

***t*-BHP/Octanal Products.** The higher molecular weight products formed included the major product, octanoic acid (30.5% at 15 min gradually decreasing to 27.2% at 180 min) and its *tert*-butyl (0.1%) and methyl (0.1%) esters. Other condensation products included heptyl *tert*-butyl ether (0.4-0.9% at 120 min then decreasing to 0.5% at 180 min) and heptyl *tert*-butyl peroxide (increasing to 0.4% at 180 min).

Octanoic acid can arise from several mechanisms. Among these are the following: nucleophilic reaction of the aldehyde with *t*-BHP, the reaction of the octanoyl radical with molecular oxygen, the reaction of the octanoyl radical with *tert*-butyl peroxy radical, or the reaction of an octanoyl radical with *t*-BHP to yield the acid and the alkoxy radical.

A series of 15-min reactions were run as described except a radical scavenger (1,4-cyclohexadiene) was added in 0.05-mmol increments. For the 15-min runs containing 0.15 mmol of 1,3 cyclohexadiene, scavenging was practically complete. Product yields found were 9.7% octanoic acid, 1.0% carbon monoxide, 1.2% heptane, 0.2% *tert*-butyl alcohol, 0.1% isobutylene, and only a trace of the other products shown in Table I. A nonzero limiting yield for the octanoic acid suggests that the radical paths to the acid were responsible for most but not all of its yield. The decreasing yield of the acid at 180 min showed that it was undergoing secondary reactions at this long time period. The octanoic acid once formed can react by several avenues. Among these are the formation of esters; both the *tert*-butyl and methyl esters were found. The α-hydrogen of an acid or ester is labile to attack by free radicals. The

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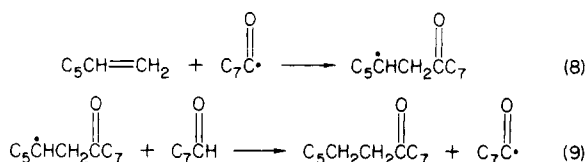
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radical formed can add to an olefin, thus leading to branched C₁₅ acids or esters as products. These substances were found in trace amounts at all reaction times.

The *tert*-butylperoxy radical was the least reactive and most plentiful radical present in the system.⁸ This would make a termination step involving this radical and a heptyl radical a probable reactive pathway, thus accounting for the observed peroxide product. A like termination step involving the *tert*-butoxy radical was not expected since the reactivity of the alkoxy radical would preclude such a step. Consequently, the heptyl *tert*-butyl ether was most likely the result of an S_H2 type reaction.

The heptyl radical was observed to undergo dimerization to yield a trace amount of tetradecane(s).

The olefin, heptene, was not only involved in lower molecular weight products but can be implicated in the higher molecular weight products as well. Heptene can react by the addition of an acyl radical (steps 8 and 9).



The resulting ketone (8-pentadecanone) was a minor product at all reaction times but increased slightly as reaction time progressed.

Solvent Products. The major products that were observed from solvent participation are toluene (0.1% at 15 min to 0.3% at 180 min) and *n*-heptylbenzene (0.3% at 15 min to 1.0% at 180 min). No xylenes or other substituted benzenes were found regardless of reaction time.

The yield of toluene was uniformly low at all reaction times. This was in keeping with the low yield of acetone that was observed from the cleavage of *t*-BHP. The methyl radical also arises from this step. The small amounts of methane, ethane, and isomeric methylheptanes would give expectations for low yields of other methyl radical products.

The heptyl radical was generated in greater yield than any other alkyl radical in the system. Consequently, a higher yield was found for *n*-heptylbenzene than for toluene.

Experimental Section

Reagents. *tert*-Butyl hydroperoxide (*t*-BHP) (90%) obtained from Aldrich Chemical Co. was distilled in vacuo to 99.9% purity. Octanal was synthesized and purified likewise to 99+% purity.¹² 1,4-Cyclohexadiene was obtained from Aldrich Chemical Co. and used without further purification.

The benzene solvent (Fisher certified) was refluxed over CaH₂ and distilled.

Method. The reactions were carried out in sealed borosilicate glass tubes. The reagents (typically 0.4 mmol of *t*-BHP and 0.8 mmol of octanal in 0.7 mL of benzene solvent) were weighed into 6-in. long, 1/4-in. o.d. Pyrex tubes closed at one end and fitted at the other with a stainless-steel valve via a Swagelok (teflon ferrules) fitting. The tube was attached to a vacuum system, cooled to -78 °C, and subjected to several freeze-pump-thaw cycles. The tube was then subsequently flame sealed below the valve. The ullage volume (0.30 mL) was kept constant for all runs. The deaerated samples were warmed to room temperature and immersed in a Cole-Parmer fluidized sand bath. The temperature (140 °C) was controlled by a Leeds and Northrup Electromax III temperature controller. The total pressure during each run was estimated to be 5.1 atm. After the reaction period, the sealed tube was cooled to 77 K and opened. The tube was capped and warmed to room temperature, and the internal standards were

added. The solution was transferred to a screw cap vial (Teflon capliner) and stored at 0 °C until analysis. Since a typical chromatogram required 60 min, two internal standards were utilized. One, ethyl benzene, afforded quantitation for the peaks with short retention times and a second, 1-phenyldodecane, for the peaks with longer retention times.

Samples were heated for time periods of 15, 30, 60, 120, or 180 min. All tubes were subjected to the same cleaning procedure. They were filled with toluene, cleaned with a nylon brush, rinsed with toluene twice and then with methylene chloride, and dried in air at 150 °C for 8 h. A search of the literature gives a few examples of catalytic behavior with glass systems,^{6,13,14} however, when a glass tube was partially filled with crushed Pyrex, thus increasing the surface area, the results at 140 °C for the above time periods were not substantially altered.

The reactions employing the radical scavenger 1,4-cyclohexadiene were run as described except the scavenger was added in 0.05-mmol increments from 0.05 to 0.15 mmol.

The samples were analyzed by two techniques, both based on gas chromatography. Peak identification for both techniques was based on retention time matching with standards and mass spectrometry. In the first, a Varian gas chromatograph Model 3700 with flame ionization detector (FID) and equipped with a 50-m 0.21-mm i.d. wall-coated open tubular (OV-101) fused silica capillary column gave the necessary resolution to distinctly separate the individual components. A 15-m but otherwise identical column was used for octanoic acid analysis. A carrier gas flow of 1 mL/min was combined with an inlet split ratio of 60:1 and a temperature program with an initial hold at 50 °C for 8 min, a ramp of 4 °C/min, and a final temperature of 260 °C.

In the second technique, gases formed during the reaction were analyzed by using a Perkin-Elmer Model Sigma 2 gas chromatograph equipped with a 6 ft. 5A molecular sieve column for CO and CH₄ and a 4 ft. Porapak/S column for CO₂.

In this mode, the column was operated at 55 °C. The chromatogram was recorded and integrated on a Hewlett-Packard Model 3390A reporting integrator. For this procedure, the valve was left on the reaction tube and after the appropriate reaction period the tube valve was connected directly to a GC gas sampling valve via a Swagelok connection. An external standard was used for calibration. A pressure gauge measured the pressure in the sample loop at the time of analysis.

A material balance was assessed for each compound. The principal peaks of the chromatogram account for approximately 88% of the original compounds. The very small peaks account for another 7-8%. The product distribution was repeatable to 2-3% for each component.

Registry No. *t*-BHP, 75-91-2; octanal, 124-13-0.

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An Improved Synthesis of Seven-Membered, Ring-Fused 12-*s*-Cis Conformationally Locked 11-*cis*-Retinoids

Michael H. Silveira and William H. Okamura*

Department of Chemistry, University of California, Riverside, California 92521

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Retinoids (vitamin A)¹ continue to be substances of interest in a multifarious set of biological processes including those in vision,^{2a} energy transduction,^{2b} cancer

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