RICE UNIVERSITY

THE PHOTOCHEMISTRY OF SOME 
$\beta,\gamma$-ALLELIC AND ACETYLENIC KETONES

BY

YU-MIN HSIEH

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Paul D. Engel

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ABSTRACT

The photochemistry of 3,3,5,5-tetramethylhepta-1,6-diyne-4-one (4), 3,3-dimethylhexa-4,5-dien-2-one (5) and 3,3,5,5-tetramethylocta-1,6,7-trien-4-one (6) were investigated. The synthesis of 4 was carried out by alkali cleavage of the bistrimethylsilylated precursor which resulted from the reaction of phosgene and the Grignard reagent from 1-trimethylsilyl-3-methyl-3-chloro-1-butyne. Ketones 5 and 6 were prepared by reacting 2,2-dimethylpenta-3,4-dienal with MeMgI and 3-methylbut-2-enyl magnesium chloride respectively to form the corresponding alcohols, which were then oxidized to the ketones by pyridinium chlorochromate. Upon direct irradiation, 4 gave the expected \( \text{C}_{10} \) coupling hydrocarbons in a ratio similar to that obtained from thermolysis of the analogous azo compound. No turnaround (1,3-acyl shift) product was observed. Acetone sensitized irradiation of 4 gave the same hydrocarbons in a different ratio and three unidentified minor components. The difference in the ratio of \( \text{C}_{10} \) hydrocarbons was explained by a secondary process involving acetone. None of the photoreactions of 5 appeared to be very interesting. Except
for the formation of polymers, the only isolable product was 4,4,7-
trimethyl-5-methyleneocta-1,2,6-triene. The direct and sensitized
irradiation of \( \tilde{J} \) gave the same thirteen products, which indicates
that intersystem crossing in \( \tilde{J} \) is more efficient than in normal acyclic
\( \Delta, \beta \)-unsaturated ketones. The \( \lambda \)-cleavage process may also arise
from the \( T_1 \) state in \( \tilde{J} \) based on this observation. Three of the products
were \( C_{10} \) hydrocarbons from dimerization of 1,1-dimethylallyl radical
and another was 2,5-hexanediol resulting from the photoreaction
of acetone with itself. Two [2+2] cycloaddition products, tricyclo-
[3,1,1]-2,2,4,4-tetramethyl-6-methyleneheptan-3-one and bicyclo-
[3,2,0]-2,2,4,4-tetramethyl-6-methyleneheptan-3-one, were also
identified.
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INTRODUCTION

The photochemistry of $\beta, \gamma$-unsaturated ketones ($\beta, \gamma$-UK's) has been intensively studied over the past ten years. These compounds show photoreactions characteristic of alkenes, of ketones, and of both chromophores acting together. The main photoproducts are illustrated below using bis-$\beta, \gamma$-UK 1 as an example (Scheme 1).

Scheme 1:

--- process not observed in 1, --- process observed in 1

cis-trans isomerization

process not observed in 1, --- process observed in 1

radical coupling products
Although the oxetane and oxa-di-\pi -methane (ODPM) products formed in principle upon irradiation are much more strained than the starting ketone, it should be noted that sensitized irradiation also gives strained cycloaddition products. The absence of the ODPM product in the case of \( \underline{1} \) is attributable to competing facile rotation about the carbon-carbon double bond (free rotor effect).\(^1\) The requirement of an electron-rich double bond disfavors oxetane formation relative to \( \alpha \)-cleavage on direct irradiation.\(^3\) Finally, the difference between singlet and triplet photochemistry of ketone \( \underline{1} \) is readily understood on the basis of the inefficiency of intersystem crossing in \( \beta, \gamma \)-UK's.

Although the photochemistry of many carbonyl compounds with \( \beta, \gamma \)-unsaturation has been investigated, only a few of them were \( \beta, \gamma \)-acetylenic. The reported cases include ketones \( \underline{2} \) and \( \underline{3} \) studied by Engel and Schexnayder\(^2\)(cf. Scheme 2) and 2-ethynyl-cycloheptanone examined by Carlson.\(^4\)

Direct irradiation of \( \underline{2} \) gives the turnaround ketone and radical recombination products expected from the \( \alpha \)-cleavage process. However, acetone sensitized irradiation gives no reaction, possibly because of an unfavorable geometric factor for the formation of ODPM product (a cyclopropene structure). Whereas ketone \( \underline{3} \) gives the usual \( \alpha \)-cleavage process on direct irradiation, it undergoes intramolecular cycloaddition on sensitized irradiation.
Scheme 2:
no reaction

The photoreactions of $\beta,\gamma$-allenic ketones are completely unexplored; in fact, the 1966 monograph by Calvert and Pitts\textsuperscript{5} mentions nothing about any type of allene and only a handful of photochemical studies on these compounds have been carried out since then.\textsuperscript{6-8}

This thesis explores the photochemistry of compounds 4 to 6.
One possible photoreaction for ketone 4 (cf. Scheme 3) on direct irradiation is ω-cleavage, which will give the turnaround ketone, carbon monoxide and the coupling C_{10} hydrocarbons from 1,1-dimethylpropargyl radical. Compound 4 may be a more convenient source of 1,1-dimethylpropargyl radical than the analogous azo compound, which decomposes badly upon storage. 9

Scheme 3:

By analogy with the behavior of 2 and 3, the acetone sensitized irradiation of 4 (cf. Scheme 4) may lead to intramolecular [2+2] cycloaddition to form a very strained anti-aromatic species, the cyclobutadiene derivative II. These highly unstable compounds can be prepared successfully by only a few routes. 10 In one case, a cyclobutadiene was isolated and identified as compound 8. 11 Although
Scheme 4:

\[ \text{Scheme 4:} \]

\[ \text{\( \sim \) may form a dimer or be trapped with either maleic anhydride or metal complex, it is quite interesting to note that both \( \sim \) and \( \sim \) possess a heavily substituted cyclobutadiene ring (compound \( \sim \) may result from sensitized irradiation of the precursor of \( \sim \)). Isolation of \( \sim \) therefore seems possible.} \]

\[ \text{Direct irradiation of} \sim \text{ is likely to give the delocalized radical} \]

\[ \text{10, which on recombination with the acetyl radical may provide a synthetically useful transformation to the} \text{ \( \sim \)-dienic ketones.} \]
Analogous to this rearrangement is the irradiation of 11, which resulted in a 1,3-migration of bromine by a free radical path. 12

Another possible product from direct irradiation of 5 is the oxetane.

Although \(\alpha\)-methylene oxetanes exist despite their high strain
energy, this product may not form because of the high ionization potential of allenes. The ODPM product of could be a methylenecyclopropane or an epoxide, though the latter is unprecedented. Since allenes possess a triplet state at about 60 kcal/mole and are capable of rotation about the double bond, the free rotor effect is expected to preclude the ODPM rearrangement.

Direct irradiation of compound should not give any photoreactions which have not already been discussed, but the sensitized irradiation could be very interesting. In view of the behavior of and, may give four different products from direct and crisscross cycladditions.
This study has the following purposes: (1) To expand our knowledge of $\beta, \gamma$-UK photochemistry to include $\beta, \gamma$-allenic ketones. (2) To study ketone 4 which completes the series started by compounds 1 and 3. Although the latter show intramolecular [2+2] cycloaddition, formation of cyclobutadiene by acetylene dimerization is unprecedented. (3) To reveal the importance of electronic, geometric and energetic factors in intramolecular allene photodimerization. (4) To understand the behavior of delocalized allenyl radical 10 in comparison to simple allyl and propargyl radicals. (5) To synthesize some interesting strained compounds.
SYNTHESIS OF COMPOUNDS

All attempts to make ketone 4 in this laboratory had failed until the synthesis below (cf. Scheme 5) was accomplished in 1977.

Scheme 5:

\[
\begin{align*}
\text{EtMgBr} & \quad \text{Me}_3\text{SiCl} \\
\text{HCl, } \text{H}_2\text{O} & \quad \text{conc. HCl} + \text{ZnCl}_2
\end{align*}
\]

The key step of this synthesis is the formation of Grignard reagent 16 using Riecke's activated magnesium,\(^\text{17}\) which is very reactive even at -78°C. This Grignard reagent was then reacted with phosgene at -78°C to give the bis-trimethylsilylated ketone 17 which was converted to 4 by alkaline cleavage.\(^\text{18}\)

The synthesis of 5 and 6 was carried out without difficulty by reacting aldehyde 18 with different Grignard reagents to form the corresponding alcohols (cf. Scheme 6). These alcohols were
then converted to the ketones by pyridinium chlorochromate oxidation.\textsuperscript{19}

Scheme 6:
Although it would be preferable to have authentic samples of the photoreaction products, their synthesis has not been completed yet because of limited time. However, the first three steps in the preparation of 4b are included in the experimental section (cf. Scheme 7).

Scheme 7:

\[
\begin{align*}
\text{1. } & 
\text{EtMgBr} \quad \text{(1)} \\
\text{in THF} \\
\text{2. } & 
\text{HCHO} \quad \text{(2)} \\
\end{align*}
\]
RESULTS AND DISCUSSION

Direct irradiation of \( \sim \) gave the three \( C_{10} \) hydrocarbons \( 4c, 4d \) and \( 4e \) in the ratio of 19 : 68 : 13, which is similar to that obtained (33 : 57 : 10) from thermolysis of the analogous azo compound.\(^9\) Turnaround ketone \( \sim 4b \) was not present in the photolysate, a surprising observation in view of the frequency with which such products are found in \( \beta, \gamma \) -UK photochemistry.
One postulate which might explain this result is that \( \alpha \)-cleavage involves buildup of positive charge at the leaving alkyl carbon.

\[
\text{R} - \text{C} = \text{R} \xrightarrow{h\nu} \left( \text{R} \cdot \cdot \cdot \text{C} = \text{R} \leftrightarrow \text{R} \cdot \cdot \cdot \text{C} = \text{R} \right)
\]

This idea has been set forth\(^2\) to rationalize the absence of allenic turnaround ketone from \(3\) and it has received experimental support in the deoxybenzoin series.\(^{34}\) On account of its electron-withdrawing nature, the triple bond should disfavor \( \alpha \)-cleavage of the propargylic moiety (process II).
However, when only a propargylacyl radical can form, as in 4, loss of CO should be exceptionally facile because this reaction should be aided by electron withdrawal. Thus 4a decarbonylates before it undergoes much radical recombination whereas 1a survives long enough to give turnaround ketone.

Unfortunately, the fact that 3b is produced from 3 with the same quantum yield as 1b is produced from 1 discredits this idea.

The second possible explanation is that 4a reacts much faster at the tertiary end of 1,1-dimethyl propargyl radical than at the allenyl end. Although this idea is supported by esr, which says there is a greater spin density on the tertiary end than on the allenyl end of the propargyl radical, did give the turnaround ketone.
In order to explain this inconsistency, one must invoke a special electronic factor which prevents the formation of $4b$ but not $2b$. This may arise from positive charge character on the acyl radical center created by the electron-withdrawing acetylenic group.

Although the above explanations are based on the $\lambda$-cleavage process, the possibility that turnaround products arise from a concerted 1,3-acyl shift can not be ruled out. However, it is not apparent why the 1,3-acyl shift should not operate in $4$. Since none of the possible explanations is consistent with all of the results, more experiments are required in order to unravel this complicated problem. These include the measurements of CO quantum yield and singlet lifetime, and possible trapping experiments for acyl radical $4a$.

Sensitized irradiation of $4$ gave, besides the three $C_{10}$ hydrocarbons, several other minor, unidentified components (column A, 100°C, retention times: 15 min., 17.1 min., and 20.4 min.). The ratio of $4c$ to $4d$ (see p. 13) increased with time and at the end of the reaction, a value of $2.58 : 1$ was obtained. Comparison of this value to that from direct irradiation ($4c : 4d = 1 : 3.57$), shows clearly that some secondary photoprocesses involving the acetone (solvent) molecules took place.

Irradiation of $5$ in benzene gave $5a$ as the only isolable product,
but with low quantum efficiency and yield. The amount of 5a formed was only about 1.6% of the starting material at the end of the reaction (80% conversion of $\sim$). There were three unidentified minor products with gc retention times of 23.1 min., 35.1 min. and 64.5 min. on column E, 89°C.

It is very likely that the delocalized radical $10$ also gave coupling hydrocarbons 5a and 5b which possibly were two of those unidentified products. By comparison of these products to those obtained from 1,1-dimethylpropargyl radical, the interesting observation is that both of the major products (5a, 4d) resulted from tail to head recombination of the corresponding radical.
In the propargyl case, this result was explained in terms of the influences of both setric and electronic factors (i.e. greater spin density at the tertiary end) on the recombination. By analogy to that, one may conclude that there is also a greater spin density at the tertiary end than at the vinyl-allyl end of 10.

The concentrated product solution of 5 after sensitized irradiation was yellow, but no products were detectable by gc or tlc. Probably, polymerization was the only process for the consumption of 5.

\[
\begin{array}{c}
\text{hv} \\
\text{polymer}
\end{array}
\]

Direct and sensitized irradiation of 6 gave the same mixture of products using comparable irradiation times (approximately 2 hours). This is an interesting result because it reveals that intersystem crossing in 6 is somewhat more efficient than in normal acyclic \( \beta, \gamma \)-UK's. The \( \alpha \)-cleavage process may also result from the T1 state, according to this observation. Six of the 13 products formed were identified using either the gc retention time or spectral data as shown in the following scheme.
Finally, the following table provides some spectral properties of 4, 5 and 6. $\Phi_f$ for 4 is unusually high$^{20}$ which is in accord with the postulate of a polar effect$^{34}$ on $\alpha$-cleavage of $\beta, \gamma$-UK's.

<table>
<thead>
<tr>
<th>Compound</th>
<th>UV absorption $\lambda_{\text{max}}$ (nm), ($\epsilon$)</th>
<th>Fluorescence $\lambda_{\text{max}}$ (nm)</th>
<th>$\Phi_f$</th>
<th>$E_g$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>306, (129)</td>
<td>400</td>
<td>3.24x10$^{-2}$</td>
<td>86.9</td>
</tr>
<tr>
<td>5</td>
<td>298, (133)</td>
<td>400</td>
<td>1.89x10$^{-3}$</td>
<td>86.4</td>
</tr>
<tr>
<td>6</td>
<td>308, (57.5)</td>
<td>400</td>
<td>3.57x10$^{-3}$</td>
<td>84.6</td>
</tr>
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EXPERIMENTAL

General

Nmr spectra were run on a Varian EM390 Nmr spectrometer. Fluorescence and phosphorescence spectra were taken on a Perkin-Elmer model MPF-2A fluorescence spectrometer. Uv absorption spectra were recorded on a Cary 17 spectrometer. High resolution mass spectra were run on a Du Pont CEC 21-110 mass spectrometer. Ir spectra were run on a Beckman IR 8 infrared spectrometer using polystyrene (1601 cm\(^{-1}\)) or acetone (1715 cm\(^{-1}\)) as a reference. A Hanovia 450W mercury lamp with a pyrex filter sleeve was the light source in all photochemical experiments. Elemental analysis was carried out by Elek Microanalytical Laboratories, Torrance, California.

Analytical gc was performed on a Hewlett-Packard F & M Scientific 700 chromatograph (thermal conductivity detector), utilizing the following columns:

- A: 25 ft. x 1/8 in. x 10%, Apiezon L
- B: 10 ft. x 1/8 in. x 15%, XE60
- C: 15 ft. x 1/8 in. x 5%, OV-17
- D: 30 ft. x 1/8 in. x 30%, Apiezon L
- E: 12 ft. x 1/4 in. x 15%, DEGS.

All of the column packings were made on chromosorb P (60-80 mesh).

Preparative gc was performed on column E with the same chromatograph using an auxiliary heater on the exit port.

Materials

Reagent grade commercial chemicals were used without further
purification, except for the following: Acetone (Mallinckrodt) for sensitized irradiation was dried with $K_2CO_3$ and distilled before use. Benzene (Mallinckrodt) was distilled from sodium for use in direct irradiation. Anhydrous ether (Mallinckrodt) was dried over sodium for all the Grignard reactions. Isobutyraldehyde (Aldrich) was distilled from $K_2CO_3$. Pyridine (Fisher) was distilled from sodium and stored over 4 Å molecular seive. THF (Aldrich) was purified according to the procedure of Bercaw and Garrett using sodium and benzophenone. $N_2$ was purified by a gas train with the following traps arranged in series: an oxygen absorbent ($LiAlH_4$ - triphenyl methane-pyridine), an empty trap, two concentrated sulfuric acid traps, an empty trap, solid sodium hydroxide tower and finally a cold empty trap (-78°C).

Photoreactions

(A) General procedures

(1) Small scale irradiations

About 10 mg of each sample were mixed with 1 ml of solvent (benzene or acetone) in a 7 mm pyrex glass tube. The solution was degassed by three freeze-thaw cycles at $10^{-4}$ mm and the tube was sealed. The tubes (several tubes for different irradiation times) were fastened by two rubber bands onto the outside of a single-walled pyrex photoreaction vessel. The whole assembly was immersed in
a water bath cooled by a copper coil with cold water running through it. The reactions were run without any other filters. After the desired time of irradiation, the tube was withdrawn and examined by gc and tlc.

(2) Preparative irradiations

About 3 g of each sample were mixed with 350 ml of benzene or acetone in a vessel with three side arms for (a) a dry ice reflux condenser, (b) a nitrogen bubbler and (c) a septum for withdrawing aliquots. The lamp and cooling jacket were fitted into this irradiation vessel and the whole apparatus was placed in the same water bath as described previously. The solution was purged with purified nitrogen (see materials) for one hour prior to irradiation and also throughout the irradiation period. Periodically, aliquots were withdrawn and examined by gc. Irradiation was halted when 80% of the starting material was consumed.

(B) Determination of fluorescence quantum yields

Solutions of compounds 4, 5, 6 and zone refined phenanthrene were prepared in hexane (spectrograde) and the absorbances at 310 nm were measured. Examination of the hexane alone showed no emission in the wavelength region of interest. Fluorescence spectra were recorded for all the samples under exactly the same conditions (excitation slit, 4; excitation λ, 310 nm; sensitivity: 6). Each sample
was run three times and three xerox copies of these spectra were made. The absorbances at 310 nm and the weights of the area under the fluorescence curves were measured (phenanthrene, 0.116, 2.5251 g; \( \gamma \), 0.242, 2.0692 g; \( \zeta \), 0.127, 0.1381 g; \( \delta \), 0.330, 0.2060 g). The quantum yields of fluorescence of samples \( \gamma \), \( \zeta \) and \( \delta \) were calculated relative to that of phenanthrene\(^{33} \) by the following equation:

\[
\Phi_f = \frac{W \times K}{I_0 (10^{-1/2}A)} , \quad \Phi_{f, \text{ph.}}^{33} = \frac{0.13}{3.8}
\]

where \( W \) = weight of the area under the fluorescence spectra
\( K \) = proportionality constant
\( I_0 \) = light intensity before passing through the sample
\( A \) = absorbance

(C) Analysis of photoproducts

At the end of all the preparative irradiations, the solvent was removed by distillation through a one ft. Vigreux column under reduced pressure. The remaining solution (approximately 10 ml) was analysed and the products were separated by tlc, gc and lc.

One of the three \( C_{10} \) coupling hydrocarbons (\( \gamma \)) from recombination of 1,1-dimethylpropargyl radical was identified by comparing the gc trace of the concentrated photoreaction solution with that of an authentic sample \(^{24} \) and with the photoreaction product from the analogous azo compound\(^{20} \) on columns A, B, C and E, which
showed exactly the same retention time for this compound. The other two C\textsubscript{10} hydrocarbons (4c and 4d) were identified by comparing the spectral data of the samples obtained from preparative gc of the irradiation product to those from the literature.\textsuperscript{2} ( ) data obtained from literature

4c: nmr, 1.27 (1.37), s, 12 H; 2.03 (2.02), s, 2H.

   ir, 3270 s (3325 s).

4d: nmr, 1.27 (1.28), s, 6 H; 1.70 (1.70), d, J = 3 hz, 6 H; 1.95 (1.98), s, 1 H; 5.06 (5.05), m, 1 H.

   ir, 3328 s (3330 s), 2125 w (2116 w), 1975 w (1968 w).

In the case of direct irradiation of 4, the starting ketone was collected by preparative gc and examined by nmr and ir in order to find out if there was a coincidence of gc retention time between the rearranged ketone 4b and the starting one. It was concluded that no turnaround product (4b) was present.

The coupling hydrocarbon (5a) from direct irradiation of 5 was separated from the product mixture by preparative gc and identified by nmr and ir (1955 cm\textsuperscript{-1}, s; 1617 cm\textsuperscript{-1}, m).

The three C\textsubscript{10} allyl dimers were identified by comparing the gc retention time with authentic samples\textsuperscript{26} on column D, 124\textdegree C. Two of the rearrangement products (6a, 6b) were purified by lc using a 3 ft. x 3/4 in. silica gel column (230-400 mesh) and CCl\textsubscript{4} as eluent. This solvent eventually caused the lc pump to freeze
up and is therefore not recommended for general use. Product 6c was separated by preparative gc of the appropriate lc fractions. The three products were eluted in the following order: 6a, 6b and 6c. All the structure assignments of these compounds were made based on nmr and ir:

6a: 1731 cm\(^{-1}\), s.; 1675 cm\(^{-1}\), m.; 765 cm\(^{-1}\), m.
6b: 1705 cm\(^{-1}\), s.; 1677 cm\(^{-1}\), m.; 765 cm\(^{-1}\), m.
6c: 1715 cm\(^{-1}\), s.

**Synthesis of compounds**

(A) Preparation of 3,3,5,5-tetramethylhepta-1,6-diy-4-one (4)

(1) 1-trimethylsilyl-3-methyl-1-butyne-3-ol\(^{16}\) (14)

In a dry 2 1 three-necked flask equipped with mechanical stirrer, reflux condenser, addition funnel and nitrogen inlet was prepared a solution of 125 g (0.94 mol) EtMgBr in 300 ml of anhydrous ether. The dark-black mixture was stirred for one hour after the addition of EtBr. A 38.6 g (0.46 mol) portion of 2-methyl-3-butyn-2-ol was then added dropwise with ice bath cooling. The mixture turned gray with suspended solid. It was stirred for two hours until no further gas evolution was noted and then dropwise addition of 100 g (0.92 mol) of Me\(_3\)SiCl was carried out with
occasional cooling at $0^\circ$C. The gray suspension was refluxed for eight hours, then 20% HCl was added until the mixture was acidic. The layers were separated and the water layer was extracted twice with ether. The combined ether extracts were washed with saturated Na$_2$CO$_3$ solution until neutral and then they were dried over MgSO$_4$. Removal of the solvent by rotary-evaporation and vacuum distillation of the crude mixture gave 67.9 g (0.435 mol, 94.5%) of desired alcohol. The distillate solidified in the receiver, bp 63°C/10 mm (literature bp 63°C/10 mm). IR: 3615 cm$^{-1}$, s; 2162 cm$^{-1}$, m.

(2) 1-trimethylsilyl-3-methyl-3-chloro-1-butyne$^{16} (15)$

A solution of 312.2 g (2.0 mol) 1-trimethylsilyl-3-methyl-1-butyln-3-ol (14) in a minimum amount of ether was added dropwise with stirring at $0^\circ$C to a Lucas reagent prepared by dissolving 240 g of anhydrous ZnCl$_2$ in 300 ml of concentrated HCl. After the addition was complete, the dark-orange mixture was stirred for two hours and the layers were separated. The aqueous layer was diluted with 2 l cold water and was extracted with three 100 ml portions of ether. The combined ether solution was washed with saturated NaHCO$_3$ solution until neutral and dried over MgSO$_4$. The solvent was removed by rotary-evaporation and the crude product was fractionated in vacuo giving 279.4 g (1.60 mol, 80%) of the chloride, bp 41-43°C/9 mm (literature bp 52-54°C/10 mm). IR: 2164 cm$^{-1}$, m.
A mixture of 91.0 g MgCl₂·xH₂O (Alfa, technical grade), 96.8 g KI (0.583 g-atom, oven dried) and 21 anhydrous THF were placed into a 5 L three-necked flask equipped with mechanical stirrer, reflux condenser, addition funnel and nitrogen inlet. The mixture was refluxed at 80°C while 67.8 g (1.74 g-atom) of freshly cut potassium (washed with pentane) was added. The reaction mixture turned black after refluxing for a half hour. It was stirred further for two hours and then cooled in a dry ice-acetone bath. Next 35 g (0.2 mol) of 1-trimethylsilyl-3-methyl-3-chloro-1-butyne (15) in 200 ml THF was transferred into the addition funnel via syringe and the solution was added to the activated Mg at a rate of 1 drop every 5 seconds. Formation of the Grignard reagent was most successful under conditions of low temperature, vigorous stirring and slow addition of the halide using a constant rate addition funnel. If the mole ratio of activated Mg to 15 was reduced to 2 : 1, the rate of addition of 15 must be 1 drop every 70 seconds in order to obtain good yield. The reaction was examined by gc (column D, 115°C, retention times: THF 16.2 min., 1-trimethylsilyl-3-methyl-1-butyne 20.1 min., 15 26.1 min.) 10 minutes after the addition of 15 was completed, which showed that almost all the halide was consumed. The water reflux condenser was replaced by a dry ice condenser, then a stream of phosgene was passed.
slowly into the Grignard reagent for 4.5 hours at \(-78^\circ\text{C}\). The progress of this step was followed by periodically withdrawing aliquots, quenching them with saturated aqueous NH\(_4\)Cl and analysing them by gc (column B, 115°C, retention time: \(\sim 7.5\) min.). The reaction mixture was warmed to room temperature and 20 ml of isopropanol was added and stirred vigorously for one hour to destroy any remaining potassium. If the isopropanol was not added, the reaction mixture would inevitably catch fire due to the reaction between potassium and water which was added next. The mixture was then worked up by adding saturated aqueous NH\(_4\)Cl until there was solid present. The inorganic salt was filtered and washed with 50 ml of ether. The combined organic solution was dried over MgSO\(_4\) and rotary-evaporated. The remaining solvent was removed by flash-distillation at 25°C/1 mm and the resultant oil was cooled in the refrigerator for one day. It was then filtered to remove the solid by-product [probably 1,6-bis(trimethylsilyl)-3,3,5,5-tetramethylhexa-1,5-diyne]. Since the product was not distillable at 100°C/1 mm, the crude material, which weighed 21.9 g, was used in the following step. Part of it was purified by preparative gc for spectral data. The yield of 17 was 64.4% according to gc.

\[\text{Ir: } 2175 \text{ cm}^{-1}, \text{ s; } 1715 \text{ cm}^{-1}, \text{ s}.
\]

(4) 3,3,5,5-tetramethylhepta-1,6-diyn-4-one\(^{18}\) (14)

A 2.0 g (35 mg-atom) portion of KOH was dissolved in a
solution containing 30 ml of 60% ethyl alcohol in water and 10 g (approximately 32 mmol) of the crude bistrimethylsilylated ketone (17). The mixture was refluxed at 80°C for 4 hours and then it was neutralized with 20% HCL. The solution was extracted with ether and dried over MgSO₄. Removal of the solvent by rotary-evaporation and fractionation in vacuo gave 3.4 g (20.9 mmol, 65.5%) yield of 4, bp 26-28°C/2.4 mm. Analysis: calculated, C 81.42%, H 8.70%; found, C 81.33%, H 8.67%.

Ir: 3317 cm⁻¹, s; 1715 cm⁻¹, s.

(B) Preparation of 3, 3-dimethylhexa-4, 5-dien-2-one (5)

(1) Isobutyraldehyde di-prop-2-ynyl acetal (19)

A mixture of 112 g (2.0 mol) propargyl alcohol, 60 g (0.83 mol) isobutyraldehyde and 20 g (0.264 g-atom) anhydrous calcium chloride was placed in a one liter flask and mechanically stirred for 12 hours. The mixture was allowed to stand for three days with occasional shaking and then it was filtered. Fractional distillation of the crude product under vacuum gave 88.8 g (0.535 mol, 64.5% based on isobutyraldehyde) of the desired acetal, bp 57°C/1.6 mm (literature bp 63-64°C/3.2 mm). Ir: 3317 cm⁻¹, s; 1040 cm⁻¹, s.

(2) 2, 2-dimethylpenta-3, 4-dienal (18)

A 125.8 g (1.13 mol) portion of isobutyraldehyde di-prop-2-ynyl acetal (19) and three drops of 85% phosphoric acid were distilled from
a 130°C oil bath through a one foot Vigreux column which was heated to 120°C by a heating tape. After eight hours, all of the low boiling components (head temperature below 130°C) had distilled. The distillate, which weighed 110.2 g, contained propargyl alcohol and aldehyde 18, which were inseparable by distillation. Therefore the mixture was mixed with a semicarbazide hydrochloride solution [from 1,000 ml H₂O, 100 g (0.896 mol) semicarbazide hydrochloride and 150 g (L 85 g-atom) NaOAc] and heated at 100°C (bath temperature) for 30 minutes to make the corresponding semicarbazone derivative. After crystallization in an ice-H₂O bath, 64 g (0.383 mol, 34% based on starting acetal 19) of the semicarbazone was obtained. The aldehyde 18 was recovered by dissolving the semicarbozone derivative in 500 ml of water and 10 drops of concentrated HCl at 50°C and stirring for 1 hour at the same temperature. The water solution was extracted with three 50 ml portions of ether and the resultant ether solution was dried over MgSO₄. The solvent was removed by rotary-evaporation and the crude material was fractionated under vacuum, which gave a nearly quantitative yield (based on the semicarbazone derivative) of 18, bp 50°C/50 mm (literature bp 139°C/1 atm). Ir: 2702 cm⁻¹, w; 1960 cm⁻¹, m; 1732 cm⁻¹, s.

(3) 3,3-dimethylhexa-4,5-dien-2-ol
A 1,000 ml three-necked flask equipped with mechanical stirrer,
addition funnel and nitrogen inlet was dried with a heat gun. A 250 ml portion of anhydrous ether and 5.69 g (0.234 g-atom) magnesium turnings were added to the flask, which was then cooled in a refrigerated bath (-30°C to -40°C). The mixture was stirred vigorously while 33.4 g of MeI was added at a moderate rate. After the addition, the black Grignard reagent was stirred for a half hour. A 18.2 g (0.165 mol) portion of 2,2-dimethylpenta-3,4-dienal (13) was added all at once to the cold solution and the mixture was stirred for one hour before working up with saturated aqueous NH₄Cl. The white inorganic salt was removed by filtration and washed with two 10 ml portions of ether. The combined ether extracts were dried over K₂CO₃, rotary-evaporated and distilled under vacuum. One gram of starting aldehyde was recovered and 15.3 g (77%) of desired product was distilled at 58-59°C/9 mm (literature bp₃¹ 64.5-65.5°C/14 mm). Ir: 3590 cm⁻¹, w; 1960 cm⁻¹, m. (4) 3,3-dimethylhexa-4,5-dien-2-one (5)

A 14.26 g portion of 3,3-dimethylhexa-4,5-dien-2-ol (20) was mixed with 15 ml of methylene chloride and the solution was added dropwise to 36.5 g of pyridinium chlorochromate¹⁹ in 250 ml methylene chloride. The mixture was mechanically stirred for three hours at ambient temperature during which time a black, sticky substance deposited on the walls of the flask. The mixture was filtered
without difficulty through a Büchner funnel and the reaction flask was rinsed with two 10 ml portions of methylene chloride, which were also filtered. The combined methylene chloride solution was dried over potassium carbonate and rotary-evaporated. Fractional distillation under vacuum gave 10.1 g (72%) of 5, b.p. 62-63/25 mm. Analysis, calculated value for C₈H₁₂O: M⁺ 124.0888. Found: 124.0888. IR: 1962 cm⁻¹ (m), 1713 cm⁻¹ (s).

(C) Preparation of 3,3,5,5-tetramethylocta-1,6,7-trien-4-one (6)

(1) 3-methyl-1-chloro-2-butene

A 200 g portion of isoprene was placed in a 500 ml three-necked flask equipped with a mechanical stirrer, gas inlet and thermometer adapter with a side arm for a calcium chloride drying tube. The flask was cooled in a refrigerated bath (-35°C to -40°C) and gaseous hydrogen chloride was passed through a concentrated sulfuric acid trap, an empty trap and finally into the isoprene, which was kept below -15°C. The reaction was followed by gc (column A, 82°C, retention times: isoprene, 5.4 min.; 3-methyl-3-chloro-1-butene, 9 min.; 21, 18 min.) or nmr. After about 4 hours, all the isoprene had disappeared, so a 0.5 g portion of CuCl was added and the solution was refluxed for 30 minutes. This procedure isomerized the tertiary chloride to primary chloride. The mixture was then stirred at room temperature with one gram of anhydrous K₂CO₃. The inorganic salts were removed by filtration and the black filtrate was distilled at
atmospheric pressure. About 50% (by weight) of the mixture boiled in the range (79°C-83°C) with evolution of HCl gas. The distillate contained isoprene, tertiary and primary chlorides. The ratio of isoprene to chlorides was determined by nmr as 37:63.

(2) 3, 3, 5, 5-tetramethylocta-1, 6, 7-trien-4-ol (22)

A 24.7 g portion of the above mixture (containing 19.6 g, 0.187 mol of the chlorides) in 70 ml anhydrous ether was added over 4 hours with vigorous stirring under nitrogen to a mixture of 47.5 g magnesium turnings and 360 ml ether at -15°C to -25°C. The reaction was usually initiated with MeMgI. After the addition was complete, the mixture was stirred in the cold for another hour. A 7.7 g portion of 2, 2-dimethylpent-3, 4-dienal (18) was added all at once and the solution was stirred until it reached room temperature. The reaction was quenched with saturated aqueous ammonium chloride, causing formation of a precipitate of inorganic salts, and worked up as in the case of compound 20. The product (22) was not purified but instead the volatile components were removed by flash-distillation at 25°C/0.6 mm for one hour. The residue was used directly in next step. In another run, the product was distilled at 59-60°C/0.6 mm and spectral data were obtained. Ir: 3580 cm⁻¹ (w), 1958 cm⁻¹ (m), 1634 cm⁻¹ (w).

(3) 3, 3, 5, 5-tetramethylocta-1, 6, 7-trien-4-one (6)
Following the same procedure for compound 5. All of the above oil (22) was mixed with 20 ml methylene chloride and the solution was added to a mixture of 35 g pyridinium chlorochromate\(^\text{19}\) and 200 ml methylene chloride. After workup, 8.1 g [65% base on starting aldehyde (18)] of ketone 6 were obtained, b. p. 41-42°C/2.7 mm.

Analysis, calculated value for C\(_{12}\)H\(_{18}\)O: M\(^+\) 178.1357, found: 138.1357. IR: 1960 cm\(^{-1}\) (m), 1695 cm\(^{-1}\) (s), 1635 cm\(^{-1}\) (m).

(D) Preparation of 4-methylpenta-2,3-dien-1-ol\(^3\) 32 (25)

(1) 3-methyl-3-(tetrahydropyran-2-yloxy)-but-1-yne (23)

A 150.3 g (l. 82 mol) portion of 2,3-dihydropyran was mixed with an equal weight of 2-methyl-3-butyne-2-ol and two drops of concentrated HCl were added. The mixture was magnetically stirred for two hours, dried with K\(_2\)CO\(_3\)-MgSO\(_4\), filtered through a Büchner funnel and distilled to give 240 g (l. 456 mol, 80%) of 3-methyl-3-tetrahydropyran-2-ol-oxybut-1-yne, b. p. 50-52°C/4 mm. IR: 3310 cm\(^{-1}\) (s), 1115 cm\(^{-1}\) (s).

(2) 4-methyl-4-(tetrahydropyran -2-yloxy)-pent-2-yn-1-ol (24)

A 21 g (0.125 mol) portion of 23 dissolved in 40 ml of dry THF was added dropwise at 0°C with mechanical stirring to 0.25 mole of EtMgBr (from 26.4 g ethyl bromide and 6 g magnesium turnings in 100 ml THF). After the evolution of gas was no longer observed, gaseous formaldehyde, generated by heating 15 g (0.17 mol) of
paraformaldehyde at 180°C-200°C in an oil bath, was passed through a 20 mm diameter connecting tube onto the surface of the stirred mixture. The reformed paraformaldehyde which tended to clog the inlet tube was vaporized onto the reaction mixture by a heat gun. The mixture was stirred further for two hours and 15 ml of saturated aqueous NH₄Cl was added. The inorganic salt was filtered off and the solvent was removed by rotary-evaporation. Further removal of solvent was carried out by flash-distillation at 25°C/0.05 mm for 30 minutes, which left 25 g oil in the pot. Since the tetrahydropyranyl group tends to migrate from a secondary or tertiary to a primary alcoholic function upon heating, the crude product was used in the following step without further purification.

(3) 4-methylpenta-2,3-dien-1-ol (25)

75 g of 24 in 150 ml of dry ether was added to a slurry of 30 g (0.79 g-atom) LiAlH₄ in 500 ml dry ether at 0°C. The mixture was then refluxed for 4 hours and decomposed with a minimum amount of cold water (added dropwise until the gray color just disappeared). The solid was filtered and washed with methylene chloride (3 x 10 ml) and the combined solution was rotary-evaporated. Fractional distillation under vacuum gave 28 g (0.29 mol, 80% based on 23) of desired product, b.p. 55-56°C/10 mm. IR: 3625 cm⁻¹ (m), 1970 cm⁻¹ (m).
REFERENCES


14. Allen, IP=10.16 eV; methylallene IP=9.57 eV. 
J. L. Franklin, "National Standard Reference Data Series", NSRDS-NBS 26
24. Sample prepared by M. A. Schexnayder in this laboratory.
25. Oven-dried MgCl$_2$ was unreactive.
26. Sample provided by M. Page in this laboratory.
0.13 = $\Phi$ of phenanthrene, unaerated.  
3.8 = ($\Phi$ unaerated/ $\Phi$ aerated) for phenanthrene.

UV absorption of

Solvent: hexane

$\epsilon_{\text{max.}} = 1.29 \times 10^2$
UV absorption of

Solvent: hexane

$\varepsilon_{\text{max}} \approx 1.33 \times 10^2$
UV absorption of

Solvent: hexane
E_max: 57.5
Excitation and emission

Solvent: hexane
Sensitivity: 6
Excitation slit: 4
Emission slit: 4
Excitation and emission of

\[ \text{Solvent: hexane} \]

\[ \text{Sensitivity: 6} \]

\[ \text{Excitation slit: 4} \]

\[ \text{Emission slit: 4} \]
Excitation and emission of

Solvent: hexane
Sensitivity: 6
Excitation slit: 4
Emission slit: 4
$\text{Me}_3\text{Si}$

reference: Benzene