PHOTOCHEMICAL REACTIONS OF BENZOPHENONE AND CYCLOHEXENE

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Michael I. am Goldberg uc 1965
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Michael D. Goldberg

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William B. Martin, Jr.

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INTRODUCTION

Aldehydes and ketones absorb weakly in the 290 mμ region of the ultraviolet spectrum, and also at 200 mμ (this wavelength region being analogous to that occurring in the spectra of olefinic compounds). The weak absorption band in the carbonyl absorption spectrum can be attributed to an $n \longrightarrow \pi^*$ transmission of a non-bonding electron on the oxygen atom to an anti-bonding π orbital in the multiple bond to give a singlet state. It is this absorption and consequent formation of an energized state which appears responsible for most of the photochemical transformation of saturated ketones in condensed (liquid) phases. After absorption, the energy may be disposed of by re-emission, by photochemical reactions such as dissociation, rearrangement and reaction with the medium, by intersystem crossing, or by internal conversion.

The fact that electromagnetic radiation could be absorbed and put to practical chemical use was realized qualitatively by Ciamician and Silber (1), and Paterno (2) in their work in the early years of the century. It was developed slightly more quantitatively by Gatteude and Draper in an empirical law stating that radiation must be absorbed to produce any photochemical effect. And it was postulated mathematically by Einstein in 1906 in the law of photochemical equivalence, which says briefly, that one molecule reacts per quantum absorbed.

Although this paper will not in general concern itself with the more theoretical and quantitative aspects of ketone photochemistry, it might be helpful to present a brief review.

A molecule that absorbe light gains energy and hence changes its position with respect to its thermodynamic equilibrium with the environment. The absorption process is not to be regarded as equivalent to simple excitation by thermal energy. Instead, all the energy of the light quantum is taken up in excitation of an electron to a higher energy (usually antibonding) orbital. This excitation of an electron that is unshared, an example would be oxygen, to a higher energy level is an $n \longrightarrow \pi^*$ transition, where n denotes the electron that is excited is one of the unshared n electrons on oxygen and π^* denotes that the excited electron goes to an unstable, so-called antibonding orbital of the carbon oxygen double bond. With reference to benzophenone, this can be represented by:

$$R_2C :: \underset{\cdot\cdot}{O} : \xrightarrow{n \rightarrow \pi^*} R_2C :: \overset{\cdot}{\underset{\cdot\cdot}{O}} \cdot$$

There is also a second type of excitation. This may cause an electron of one of the bonding orbitals (called a π orbital) of the carbonyl group to jump to a higher π^* orbital. Such transitions are called $\pi \quad > \pi^*$ and also occur regularly in substances containing double bonds

$$R_2C :: \underset{\cdot\cdot}{O} : \xrightarrow{n \rightarrow \pi^*} R_2C \overset{:}{\cdot\,\cdot}\ \underset{\cdot\cdot}{O} :$$

Since an excited molecule is in a higher energy state as a result of either the $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ transition, it is relatively unstable and hence must dispose of its excess energy in an attempt to return to thermodynamic equilibrium. Excited-state energy may be lost in one of three ways:

(1) As energy of chemical change; this would be the case if the energy level to which the molecule is raised is above that required for dissociation. Such is the case in both the gaseous and liquid phase photolysis of acetone (3, 4, 5). The investigations were carried out in the gas phase by Noyes, and in the liquid phase by Pieck and Steacie. Acetone dissociated to free radicals with a release of

energy and by a free radical mechanism produced carbon monoxide, ethene, and methane

$$(CH_3)_2\ CO \rightarrow CH_3\ CO\cdot + CH_3\ .$$

(2) As fluorescence or phosphorescence; this would be the case if the energy level to which the molecule is raised permitted it to lose energy to the surroundings in the form of radiation and then return to the ground state.

(3) As thermal energy; this would be the case if the molecule returned to the ground state by a non-radiative process. Among the possible (non-radiative) ways for the excited state to return to some sort of ground state are through conversion to a high energy isomeric form; by chemical reaction with surrounding molecules; by transfer of excess electronic energy to other molecules; or by decay through a lower energy triplet state (a triplet state has two unpaired electrons and is normally more stable than the corresponding singlet state, which is an excited state in which all the electrons are paired. The name "triplet" arises from the fact that the two unpaired electrons turn out to have three possible energy states in an applied magnetic field. Conversion of a singlet excited state to a triplet state ($S_1 \longrightarrow T_1$) is energetically favorable but

usually occurs rather slowly. Nevertheless, if the singlet state is sufficiently long-lived, the singlet-triplet change (known as intersystem crossing) may occur for a large number of the excited molecules (6)

$$\text{benzophenone} \xrightarrow{h\nu} \text{benzophenone}^{*}\ (S)$$

$$\text{benzophenone}^{*}\ (S) \begin{array}{l} \nearrow \text{benzophenone} + h\nu\ \text{(fluorescence)} \\ \rightarrow C_6H_5 \cdot + C_6H_5CO\,.\ \text{(decomposition)} \\ \searrow \text{benzophenone}^{*}(T)\text{(intersystem crossing)} \end{array}$$

Although all of these processes are possible, the fact that benzophenone only returns to ground state by means of an excited triplet state was demonstrated by Hammond and Moore (7). Their experiments were conducted with benzophenone and varying amounts of benzhydrol in benzene solutions, and they were able to prove that since no fluorescence was detected in the production of benzopinacol there must be a longer-lived state than the singlet state, the new state being the triplet

$$B + h\nu \xrightarrow{n \longrightarrow \pi^{*}} B^{1}\ \text{(singlet)}$$

$$B^{1} \longrightarrow B^{3}\ \text{(triplet)}$$

$$B^{3} + BH_2 \longrightarrow 2\ (C_6H_5)_2\ COH \cdot \longrightarrow \text{benzpinacol}$$

In summary, ketones absorb ultraviolet light and are excited to a higher energy level (excited singlet state). Although there are many possible ways of losing this energy, higher molecular weight ketones in general transfer this energy to a lower level excited state (the triplet state) by intersystem crossing. It now remains to determine how this energy is disposed of and what types of reactive processes ketones undergo in order to dispose of it.

The oldest reaction in ketone photochemistry is the reduction of benzophenone to benzopinecol by irradiation in an alcoholic solution. This reaction, which has been known for sixty years (8) was first observed with the aryl ketone benzophenone, but the range has been extended throughout the ketone family and has produced the related pinacols with excellent results. The proposed mechanism involves hydrogen abstraction from the alcohol by the excited benzophenone molecule and consists of the following steps

$$(C_6H_5)_2\,CO \xrightarrow{h\nu} [(C_6H_5)_2\,CO]^* \xrightarrow{(CH_3)_2\,COH} (C_6H_5)_2\,COH\cdot$$

$$\longrightarrow \cdot\,(C_6H_5)_2\,COH \cdot COH \cdot (C_6H_5)_2$$

with benzopinacol resulting from the dimarization of benzhydrol radicals. Bachmann has shown that photochemical formation of benzopinacol can also be achieved from benzophenone and benzhydrol (9)

$$(C_6H_5)_2\,CO + (C_6H_5)\,CHOH \xrightarrow{hv} (C_6H_5)_2\,COH \cdot COH \cdot (C_6H_5)_2$$

The mechanism is similar to that for isopropanol as the reducing agent except that now two benzhydrol radicals are formed

$$[(C_6H_5)_2CO]^* + (C_6H_5)_2CHOH \longrightarrow 2(C_6H_5)COH \cdot$$

$$\longrightarrow (C_6H_5)_2COH \cdot COH \cdot (C_6H_5)_2$$

The reduction is believed to involve the triplet state of benzophenone for the reasons presented by Hammond and Moore (7).

On the other hand, irradiation of benzophenone in the presence of oxygen with isopropanol produces no benzopinacol (the benzophenone can be recovered at the end of the reaction), acetone, and hydrogen peroxide. The reaction of oxygen and isopropanol does not occur in the absence of benzophenone, and it is assumed that benzophenone acts as a sensitizer, transferring energy from the triplet state for the oxidation of the alcohol (10).

Related reactions to the formation of benzopinacol have been reported in other solvents, although the primary step has not necessarily been found to be hydrogen abstraction.

Thus, Schonberg et.al. (11) and Kenyon et.al. (12) have reported carbon cleavage adjacent to the carbonyl group (in much the same manner as acetone dissociation) and subsequent hydrogen abstract by the stable radicals formed.

Schonberg has reported benzoyldiphenyl methane in benzene solution yields tetraphenyl ethane and benzaldehyde by a mechanism that involves decomposition of I to a benzoyl radical plus a diphenyl methyl radical, dimerization to form tetraphenyl ethane and abstraction of a hydrogen atom from I by benzoyl to form benzaldehyde

$$2\ \underset{\text{I}}{C_6H_5COCH\,(C_6H_5)_2} \xrightarrow{h\nu} \underset{\text{II}}{(C_6H_5)_2\ CHCH\ (C_6H_5)_2} + C_6H_5\ CHO$$

While according to Kenyon, deoxybenzoin undergoes
IV
photolysis to dibenzyl, benzaldehyde and didesyl by a free
radical mechanism that postulates the abstraction of hydrogen
III
from deoxybenzoin by benzoyl radicals to produce desyl radicals
and benzaldehyde

$$(1)\ \overset{\text{II}}{PhCO \cdot CH_2Ph} \xrightarrow{hv} \overset{\text{III}}{PhCO \cdot + Ph \cdot CH_2 \cdot} \rightarrow \overset{\text{IV}}{(PhCH_2)_2}$$

$$(2)\ PhCO \cdot + PhCO\ CH_2Ph \rightarrow PhCHO + PhCO\ CH\ Ph \cdot \rightarrow (PhCOCHPh)_2$$

On the other hand, hydrogen abstraction can also occur in hydrocarbon solvents, producing compounds in a manner similar to that proposed in the benzopinacol mechanism. Reactions such as

$$(C_6H_5)_2CO \xrightarrow{hv} [(C_6H_5)_2CO]^* \xrightarrow{CH_3CH_2CH_2C_6H_5} (C_6H_5)_2COH \cdot$$

$$+ CH_3CH_2CHC_6H_5 \rightarrow (C_6H_5)_2COH \cdot CHC_2H_5 \cdot C_6H_5$$

and $(C_6H_5)_2\ CO + (C_6H_5)_2\ CH_2 \rightarrow (C_6H_5)_2\ COH \cdot CH(C_6H_5)_2$

occur because the radical produced by abstraction of hydrogen is stable enough to react before dissociation (13)(14). Bowen and Horton (15) in the same type of experiment used cyclohexane as the solvent and acetone as the ketone and upon irradiation of the solution produced dimethylcyclohexyl carbinol

$$C_6H_{12} + (CH_3)_2\ CO \rightarrow (CH_3)_2\ COH \cdot C_6H_{11}$$

In an analogous reaction with n-hexane, they produced 1,1, dimethyl n-hexanol

$$(CH_3)_2CO + CH_3(CH_2)_4CH_3 \rightarrow CH_3(CH_2)_4\,COH \cdot (CH_3)_2$$

Their results indicated that from reactions of aliphatic ketones in saturated hydrocarbon solutions, the photo product is a carbinol that is a result of a combination of one acetone molecule and one hydrocarbon molecule. However the proposed mechanism depended on decomposition of the acetone (normal gas phase reaction) rather than on the abstraction of the hydrogen atom by the excited ketone.

Yang and Yang (16) reviewed Horton's results and were able to demonstrate that a mixture of acetone and cyclohexane (1:8) gave cyclohexyldimethyl carbinol (12%), -2 propanol (53%), and pinacol (15%). The presence of pinacol and 2-propanol indicated hydrogen abstraction by the carbonyl group according to the following mechanism:

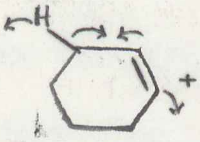
$$(CH_3)_2CO + C_6H_{12} \rightarrow (CH_3)_2COH \cdot + C_6H_{11} \cdot$$

$$\rightarrow (CH_3)_2COH \cdot C_6H_{11} + (CH_3)_2COH \cdot COH \cdot (CH_3)_2$$

$$(CH_3)_2COH \cdot + C_6H_{12} \rightarrow (CH_3)_2CHOH + C_6H_{11} \cdot$$

deMayo (17) extended these reactions using cyclohexene as the solvent in an attempt to determine if allylic hydrogens could also be easily abstracted. Reaction of acetone and cyclohexene in an oxygen-free atmosphere yielded bicyclohexenyl and cyclohexenyl dimethyl carbinal as the only products. The results indicated that allylic hydrogen abstraction was the probable mechanism (I). However, an alternate path was feasible, involving attack of the double bond with subsequent loss of a β-hydrogen atom to form a new ethylenic linkage (II). Such a mechanism has been

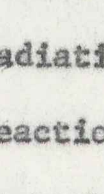
I. $C_6H_{10} + (CH_3)_2CO \rightarrow C_6H_9 \cdot + (CH_3)_2COH \cdot \rightarrow (CH_3)_2\ COH \cdot C_6H_9$

II. 

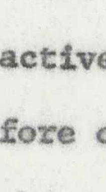
$+ [(CH_3)_2CO]^* \rightarrow (CH_3)_2 \cdot COC_6H_9 \rightarrow (CH_3)_2\ COH\ C_6H_9$

proposed in radical substitution in dienes and trienes (18)(19).

The fact that mechanism I is indeed the correct one was established by irradiation of optically active carvomenthene in acetone. The reaction was stopped before completion and the recovered carvomenthene was found to be partially racemized, indicating a symmetrical allyl radical was the intermediate

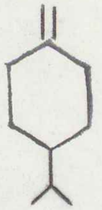


carvomenthene

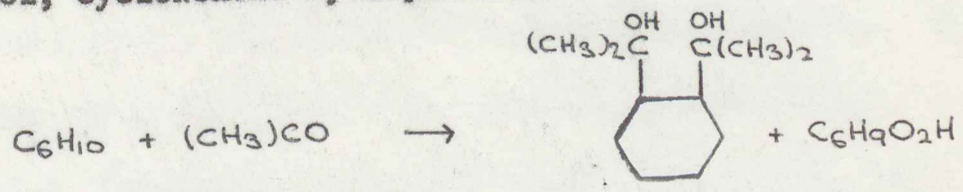


racemized product

In addition, menth-1-7-ene was found, indicating that hydrogen abstraction also occurred at the primary position



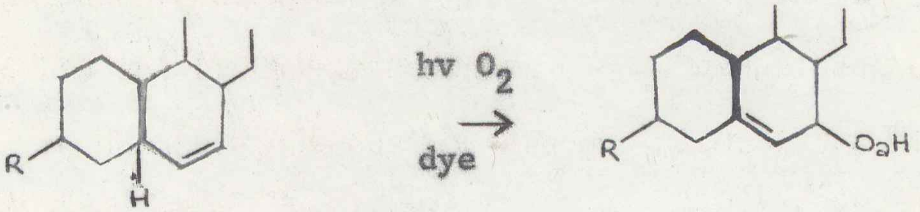
deMayo then extended his work to higher molecular weight ketones such as diethyl and di-n-propyl ketones and in each case recovered the corresponding carbinol. Finally he and his co-workers attempted the same experiment under reflux temperature, producing a second alcohol the dicarbinol and also under oxygenation (20) again producing the dicarbinol and, instead of bicyclohexenyl and dimethylcyclohexenyl carbinol, cyclohexene hydroperoxide



It was felt that the acetone underwent an additional reaction with the cyclohexene to produce the dicarbinol. As the yield was not affected by oxygen, indicating that the cyclohexenyl radical formed earlier is not an intermediate, oxetane formation was proposed as an intermediate, with subsequent cleavage due to insufficient stabilization.

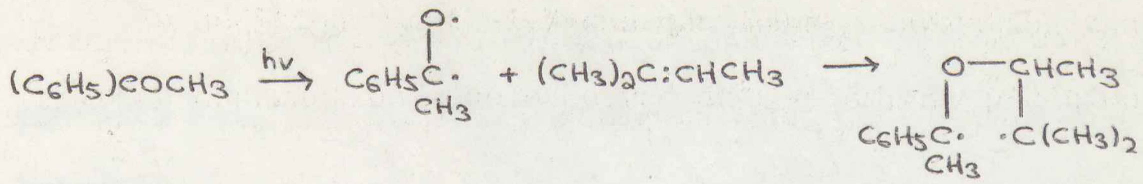
That both hydroperoxide formation and oxetane intermediaries are possible are demonstrated by the work of Nikon and Bagli on allelic hydroperoxides and by Buchi on oxetanes.

Nikon and Bagli (21) were able to oxidize olefins in the presence of a sensitizer with ultraviolet light and produce allelic hydroperoxides by a mechanism involving a shift of the double bond.



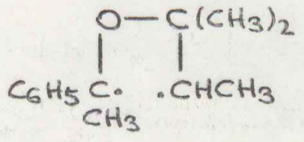
Oxetane or trimethylene oxide formation has been investigated by Buchi et al (22) who exposed heavily substituted olefins and carbonyl compounds to sunlight. The reaction of acetophenone with benzaldehyde produced 1,2,2,3,4 tetramethyl-1 phenyl trimethylene oxide, as identified from the products of cleavage of the oxetane with a mineral acid.

Their mechanism, based on the specific cleavage products involved the formation of an oxetane from a stable biradical triplet state which was the result of a collision and which preceded dissociation.



$$(C_6H_5)COCH_3 \xrightarrow{h\nu} C_6H_5\underset{CH_3}{\overset{\overset{O\cdot}{|}}{C}}\cdot + (CH_3)_2C{:}CHCH_3 \longrightarrow \begin{array}{ll} O & \!\!-CHCH_3 \\ | & \;| \\ C_6H_5\underset{CH_3}{C}\cdot & \cdot C(CH_3)_2 \end{array}$$

Rather than



$$\begin{array}{ll} O & \!\!-C(CH_3)_2 \\ | & \;| \\ C_6H_5\underset{CH_3}{C}\cdot & \cdot CHCH_3 \end{array}$$

which is less stable

In the case of insufficient stabilization, as with cyclohexene, either kharasch addition (23) or attack by an activated hydrogen may occur (to give the dicarbinol).

Heimlich (24) modified both Ciamician's (8) and deMayo's (17) work by irradiating a solution of benzophenone, isoproponol, and cyclohexene. His investigations indicated that a crystalline alcohol was produced that could be closely identified with diphenylcyclohexyl carbinol. The presence of this product indicates a distinct departure from the mechanism and products proposed by deMayo, and possibly may be attributed to a combination of both the cyclohexene and benzopinacol mechanisms.

It will be the purpose of this thesis to

1. re-run Heimlich's experiment to determine if the chclohexyl and not the cyclohexenyl carbinol is produced

2. determine whether or not steric hindrance prevents deMayo's hypothesis from being extended to aryl ketones

3. to determine if there is competition between secondary hydrogen abstraction from isopropanol and allelic hydrogen abstraction from cyclohexene.

Reactions will be run of all these reactants (benzophenone, cyclohexene and isopropanol) both with and without the presence of oxygen and of just cyclohexene and benzophenone both with and without the presence of oxygen.

EXPERIMENTAL RESULTS

All reactions listed below were carried out with benzophenone (Eastman white label) isopropanol (98-99% pure) and cyclohexene (reagent grade). In those cases (#I) where cyclohexene from a student preparation was employed, it was distilled under atmospheric pressure and the fraction having b.p. 82-83°C. was used. The Erlenmeyer and round bottom glassware used were both composed of pyrex glass and were able to transmit light effectively to 3000 A° (300 mμ). The quartz tube transmitted light to 2000 A° IR and μ-v may be taken to mean infra-red and ultra-violet spectra.

I. Photochemical reaction of cyclohexene and isopropanol respectively and benzophenone in sunlight

A quantity of the unknown was prepared according to the method of Feiser (25). Approximately equimolar amounts of benzophenone (.11 moles, 20 gms) and cyclohexene (.11 moles, 15.5 ml) were placed in both Erlenmeyer (pyrex) flasks and in round bottom flasks. Isopropanol was added to fill the flasks, corks were wired in place, and the mixtures were shaken to allow as much air as possible to come in contact with the solution. Both flasks were then inverted and placed in the sun. After three to four days, small white, rhombic crystals formed. These were separated by filtration, washed with cold isopropanol to remove impurities and dried over anhydrous $CaCl_2$.

II. Identification of cyclohexene-isopropanol-benzophenone photo product I

a. An infra-red spectrum on a Perkin-Elmer Model 21 spectrophotometer was taken of the product. A KBr disk (3% mixture of product by weight) was used. The significance of the spectrum (see Figure 1) will be discussed in the Conclusions section.

b. Melting point determinations of crystals from each of the two types of flasks yielded a temperature in both cases of 194-196°C. A mixed melting point showed no depression and also gave a temperature of 194-196°C.

c. Tests for unsaturation were carried out with bromine in carbon tetrachloride and with potassium permanganate. Both tests were negative and indicated no unsaturation.

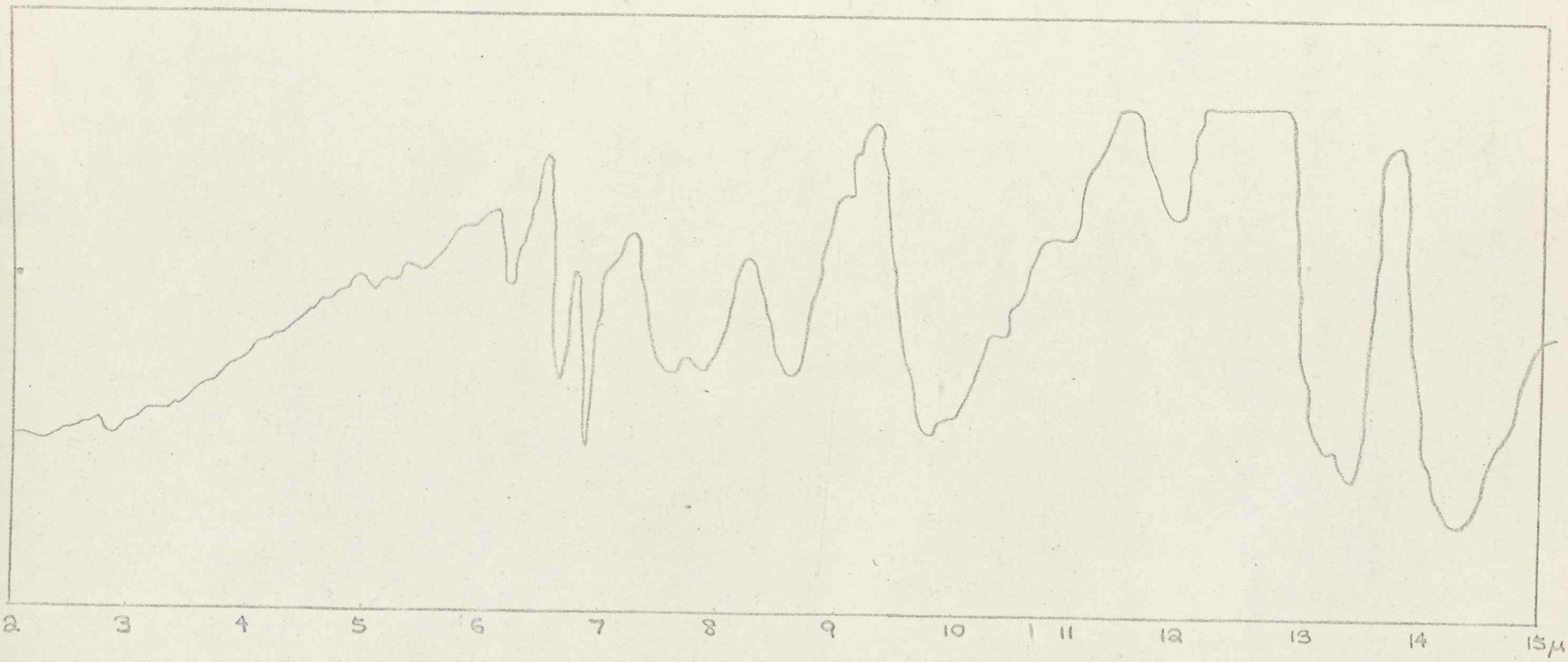


FIG I - PHOTOPRODUCT I

d. Tests for the presence of hydroxyl groups were carried out (26).

Xanthate test produced a yellow precipitate, indicating presence of an alcohol.

Lucas test for water-soluble alcohols was inconclusive.

Bordwell-Wellman test for tertiary alcohols was positive.

N-bromosuccinimide test for tertiary alcohols was positive.

e. Solubility tests

Photo product I was insoluble in cyclohexane, carbon tetrachloride, benzene, and water.

Photo product I was soluble in acetone, bromobenzene (1 gm/10 ml), and ethyl acetate.

f. Mixed melting point of Photo product I (mp 194-196) versus benzopinacol (mp 203-205) gave a melting point of 148°C. A test of photo product I with periodic acid for possible glycol structure was negative.

g. Molecular weight determination

Rast molecular weight determination with camphor as solvent in a silicone-oil bath yielded a molecular weight of 160 ± 20 (27).

Ebullometric molecular weight determination with benzene as solvent in a Cottrell apparatus (28) yielded a molecular weight of 400-500.

h. Per cent composition analysis

Experimental	C (85.08)	H (6.07)	0(9.85)(by difference)
Calculated for	C (85.6)	H (7.15)	0(7.15)
1,2 bis (α,α diphenylmethylol) cyclohexane			
Calculated for	C (85.4)	H (6.00)	0(8.75)
benzopinacol			

III. Photochemical reaction of cyclohexene-benzophenone (nitrogen saturated) in ultraviolet light

The unknown was originally prepared in much the same manner as in part I. Benzophenone (.11 moles, 20 grams) was placed in a round bottom flask and an excess of cyclohexene was added (approx. 275 ml). The flask was then flushed with nitrogen, carefully sealed and placed in the sunlight. However, as the season was winter, the extreme cold caused contraction and left a gap between stopper and flask, permitting air to enter. A new apparatus consisting of a quartz tube, an electric stirrer connected to a variac for rpm control, and a glass pipe for continuous nitrogen bubbling was therefore created for irradiations.

The solution from the round bottom flask was poured into the quartz tube. A piece of rubber dam with two holes, one for the stirrer and the other for the nitrogen inlet pipe was placed over the quartz tube to prevent air from entering. The solution was first thoroughly flushed with nitrogen to remove air bubbles present. The nitrogen was then slowed down to a rate of approximately one bubble every two seconds. Finally, a mercury arc lamp (G.E.) was placed against the side of the tube, turned on, and the reaction allowed to proceed.

Samples were removed at 24 hour intervals and subjected to analysis by I.R. The extent of hydroxyl formation was taken as a guide to the completeness of the reaction. (It should be noted that I.R. spectra for these preliminary identifications were made on solutions in NaCl cells versus a solution of the original unirradiated reactants, in a similar cell in the reference beam of the spectrophotometer) At the end of 140 hours, the reaction was judged sufficiently complete to warrant separation and identification.

IV. Identification of cyclohexene-benzophenone photo product II

The irradiated solution was first distilled under atmospheric pressure to remove the unreacted cyclohexene (b.p. 82°). An IR was taken of the residue (Figure 2).

The residue was then distilled at a pressure of 20 mm and the fraction boiling from 70-125°C. was collected. An IR was taken of the distillate (Figure 3). The distillate was removed and carefully added to an alumina chromatographic column. The following solvents were then sequentially added: petroleum ether, a mixture of 4 parts pet ether to 1 part benzene, 1 part pet ether to 1 part benzene, 1 part pet ether to 4 parts benzene, benzene, methanol, and 1 part methanol and 1 part water.

Both the pet ether fraction (II A) and the methanol fraction (II B) yielded colored (slightly yellow) solutions. These were both subjected to analysis on a Beckman D.U. μ-ɯ-visible spectrophotometer.

The petroleum ether fraction was then distilled under atmospheric pressure to remove the solvent (b.p. range 40-75°C). The residue was a greenish solution of 7 ml. An IR was taken (Figure 4).

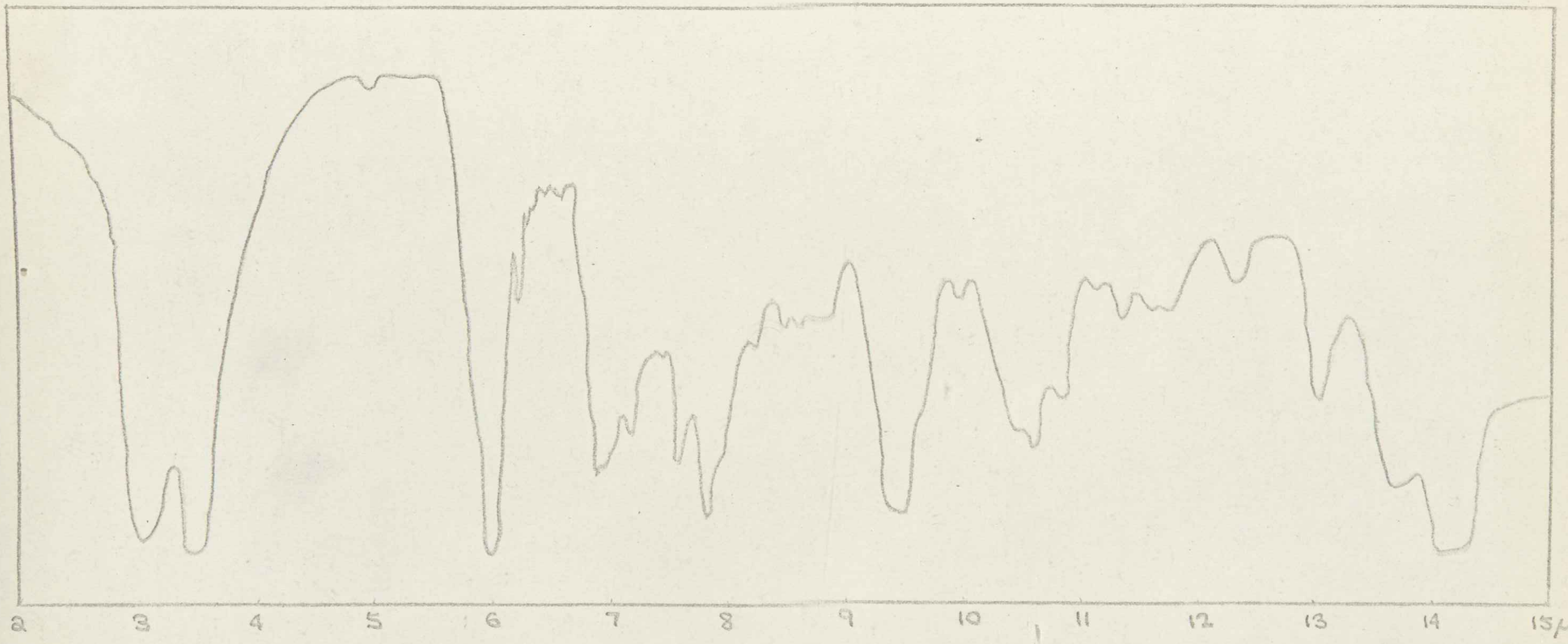


FIG II

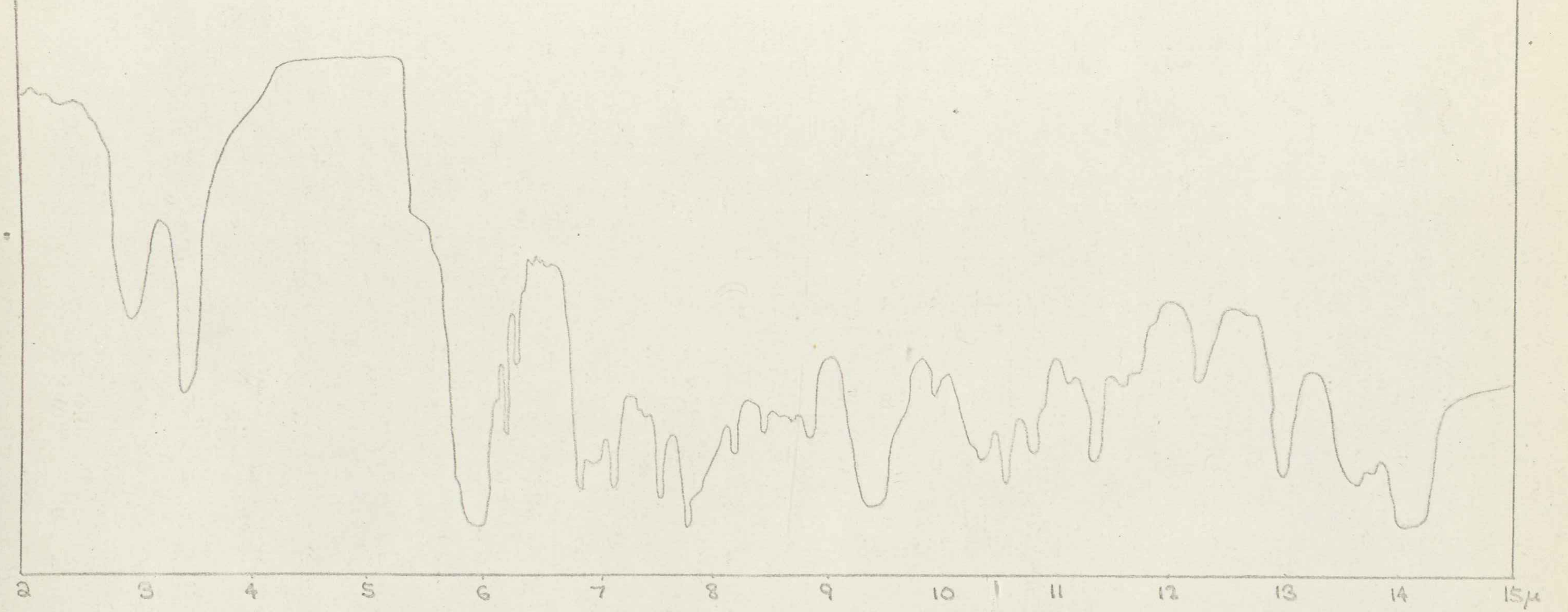


FIG III

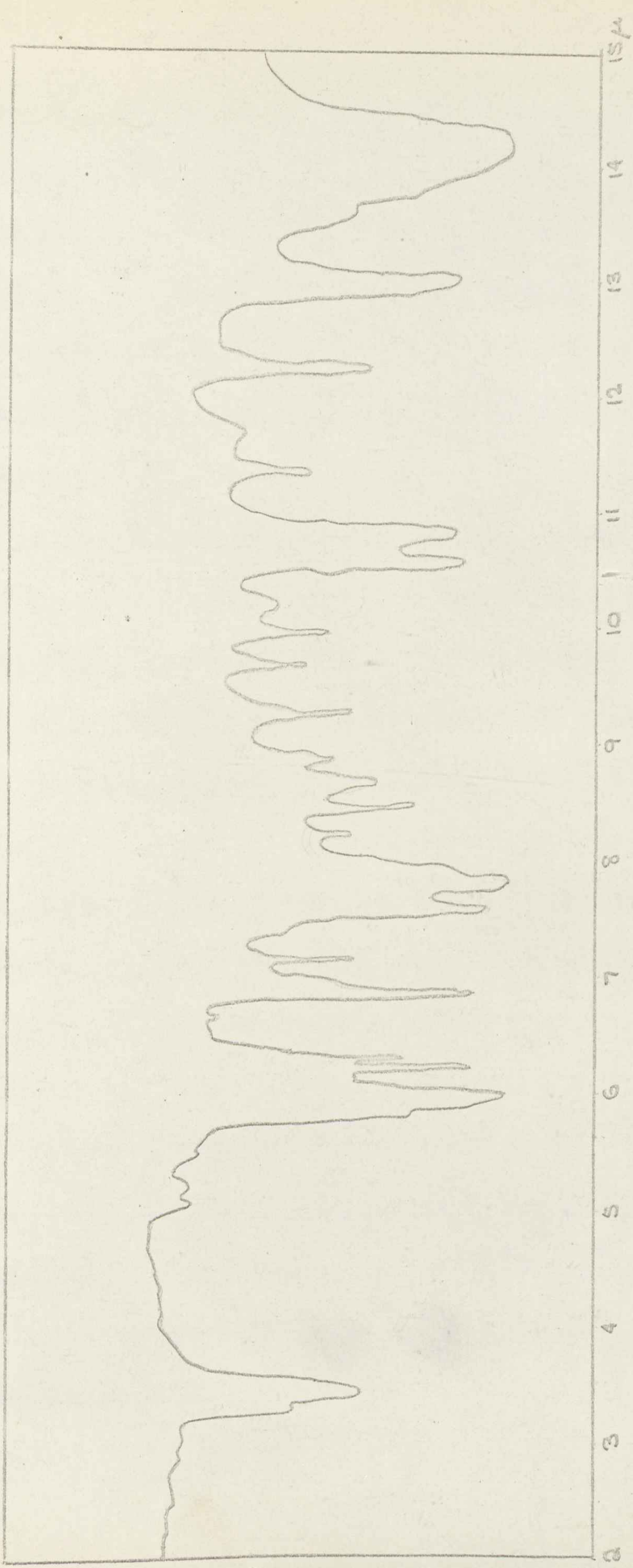


FIG IV

The residue was then distilled at a pressure of 40 mm. The material boiling at 90°C. was collected. Both IR (Figure 5) and μ-м were taken. The material remaining in the flask was washed with acetone and a white polymeric-looking material appeared.

The distillate having a b.p. of 90°C. at 40 mm. was subjected to qualitative tests:

A xanthate test for alcohol was negative.

Bromine in carbon tetrachloride and potassium permanganate tests for unsaturation were positive.

Semicarbazone test for ketones was negative.

Calcium hydride (CaH_2) test for active hydrogen was positive.

Calcium hydride test on pure cyclohexene was also positive; bubbling continued for more than one hour (a similar test on cyclohexane showed bubbling for only fifteen minutes).

The methanol fraction was tested for unsaturation (negative) and for ketone (inconclusive) before removal of the solvent by distillation. However, when distillation was carried out at atmospheric pressure, only a black tar-like residue remained.

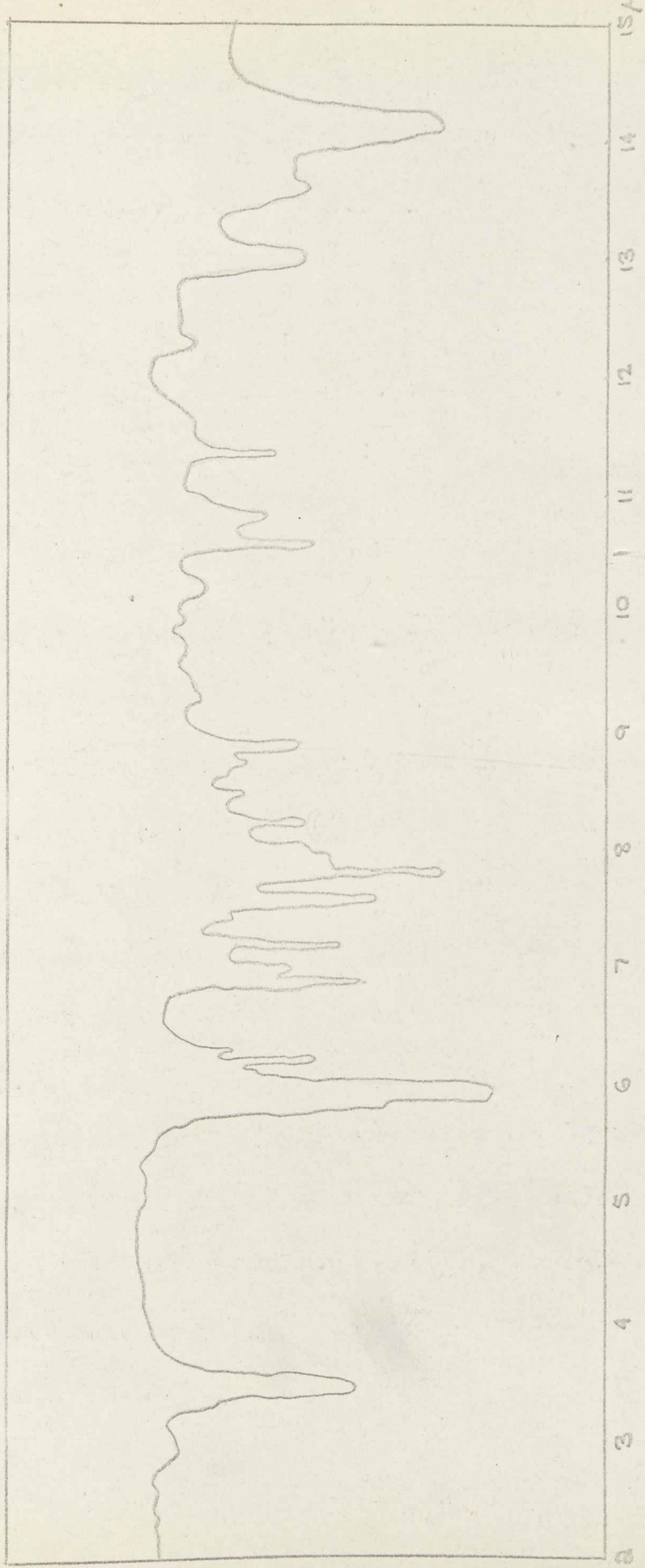


FIG V

V. Photochemical reaction from photo product III - cyclohexene-isopropanol-benzophenone (nitrogen saturated) in ultraviolet light

The reaction was again carried out in the quartz tube under conditions identical to those used for cyclohexene-benzophenone. The solution of cyclohexene (.11 moles, 15.5 ml), benzophenone (.11 moles, 20 grams) and isopropanol was irradiated for 200 hours.

VI. Identification of cyclohexene-isopropanol-benzophenone photo product III

The solution was then removed and the solvents (isopropanol and cyclohexene) distilled off. An IR was taken of the residue (Figure 6).

The residue was then distilled in vacuo at a pressure of 75-85 mm. and the fraction boiling from 80-150°C. was collected. Upon cooling, this fraction yielded large, white, feather-like crystals. The crystals were removed, dried and subjected to IR analysis and melting point determination. A mixed melting point of the crystals and benzophenone showed no depression.

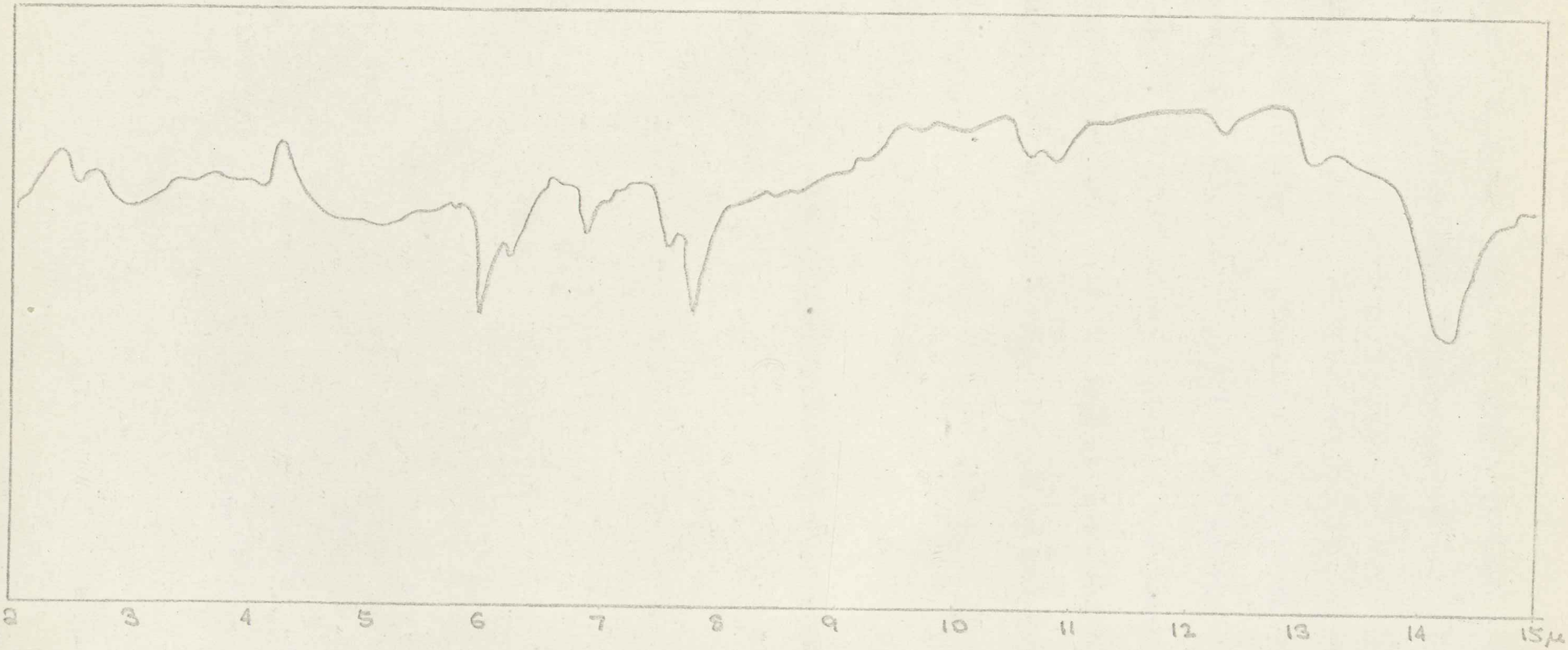


FIG VI · PHOTOPRODUCT III

VII. Photochemical reaction - photo product III from benzophenone-cyclohexene in sunlight

This reaction was carried out under the same conditions as described in part I. Benzophenone (.11 moles, 20 grams) was placed in a round-bottom flask and an excess of cyclohexene added. The flask was inverted and placed in the sunlight for three days. At the end of this period no crystals appeared but an IR (not shown) indicated the existence of several new peaks (notably at 2.85 and 6.65 μ) and the reaction was therefore stopped.

VIII. Identification of benzophenone-cyclohexene photo product IV

A new separatory procedure was adopted to insure removal of excess benzophenone (29). The entire solution was reacted with Girard's "T" reagent and refluxed for one hour. The solution was then washed with equal portions of water (to remove Girard's adduct) and ether. The water solution was removed and the ether allowed to evaporate. The ether residue was distilled to remove unreacted cyclohexene, and an IR was taken (Figure 7). The infra-red indicated the presence of a hydroxyl group (2.85 μ).

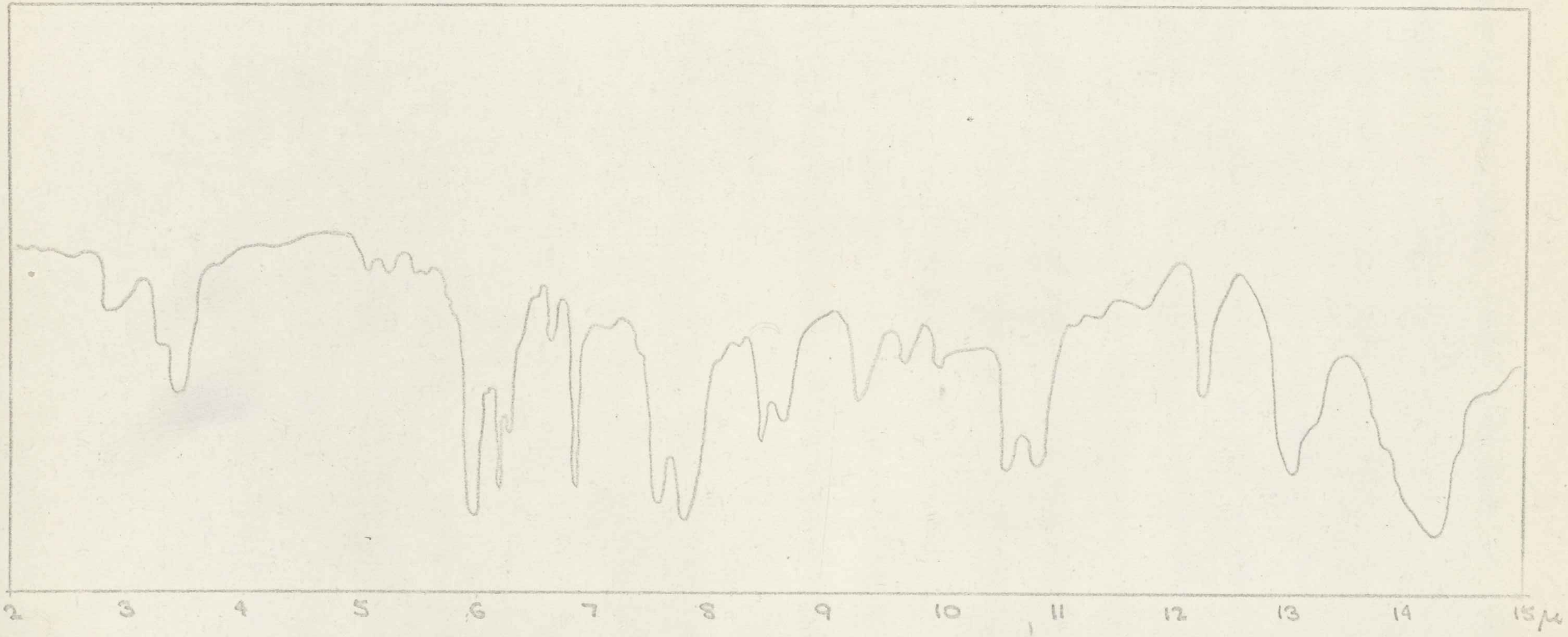


FIG VII · PHOTOPRODUCT IV

Several preliminary tests were made on the solution at this time.

Xanthate test for alcohols was positive.

Bromine in carbon tetrachloride and potassium permanganate tests for unsaturation were positive.

Upon standing overnight, a large colorless prismatic crystals separated from the solution. The supernatant liquid was poured off and the crystal was dried. An infrared spectrum and mixed melting point determination, proved that the crystal was benzophenone.

The supernatant was then adsorbed onto an alumina column and eluted sequentially by petroleum ether, methanol, and 1:1 methanol-water.

The petroleum ether fraction was evaporated over a hot plate to remove the solvent. Crystals separated from solution. Again by both IR and mixed melting point, they were proven to be benzophenone. The remaining solution was subjected to IR and to a Br_2 test for unsaturation (positive).

The methanol fraction was also evaporated over a hot plate. No crystals were found but an IR and Br_2 test were identical with those of the solution from the petroleum ether fraction. Xanthate tests for the hydroxyl group taken for both fractions were positive.

CONCLUSIONS

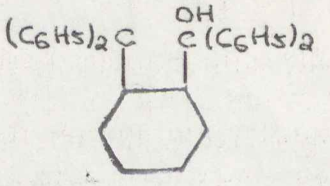
It has been noted that ketones absorb electromagnetic radiation in the general region of the spectrum extending from 2300 to 3200° A (30) and most generally at 2900°A. On the other hand, simple unsaturated hydrocarbons with one double bond only absorb effectively at wavelengths below 2200 A°. With these considerations in mind, an attempt will be made to identify and explain the existence of the products encountered in the Experimental Results section.

As can be seen from the Introduction, deMayo et al (20) have published the most recent information concerning ketone-olefin photochemistry. Leaving theoretical and mechanistic considerations aside for the moment, the reactions of ketones and olefins in ultraviolet light produce a carbinol or a dicarbinol depending upon the presence of excess oxygen. Thus, an acetone-cyclohexene preparation yields trans-1,2,Di (2'-hydroxy + 2'-propyl) cyclohexane in the presence of oxygen, and 2-cyclohex-2'-enylpropan-2-ol in the absence of oxygen. The existence of these carbinols has been confirmed by both direct structural analysis, in the form of

IR, degradation studies, etc., and by production of the same material with identical properties by a direct synthetic route. The reactions of diethyl ketone-cyclohexene and dipropyl ketone-cyclohexene have yielded analogous compounds.

In the light of these facts, it was decided to react benzophenone with cyclohexene under varying conditions in order to determine whether or not the reaction mechanism could be applied effectively to higher molecular weight and more sterically hindered ketones.

The results of the first reaction that was carried out are described in sections I and II. On the basis of the mechanism proposed and empirically confirmed by deMayo, the reaction of benzophenone and cyclohexene (in isopropanol as a solvent) in the presence of excess oxygen should yield a dicarbinol, 1, 2 bis (α, α, diphenylmethylol) cyclohexane, of molecular weight 456 a.m.u.



A general literature search for this material in both chemical abstracts and Beilstein gave no indication of its previous existence. Identification was therefore attempted by a process of elimination of all other theoretical possibilities. This necessitated the large number of qualitative tests that were undertaken and whose results are reported in part II.

Briefly, the data indicate an organic crystalline solid of high melting point and molecular weight, with no unsaturation, at least one hydroxyl group present, and solubility in polar solvents, with the exception of water.

The melting point alone rules out the possibility of the material being unreacted benzophenone $(C_6H_5)_2CO$ (mp. 49, m.w. 182). It also rules out benzhydrol $(C_6H_5)_2CHOH$ (m.p. 68, m.w., 184), although its molecular weight is close to that reported by the Rast method. The existence of the tertiary hydroxyl group, confirmed by the three qualitative tests and by an IR peak at $2.85\,\mu$ eliminates tris β phenyl acetophenone $(C_6H_5)_3CCO \cdot C_6H_5$ (m.p. 179-80, m.w. 348) and the oxetane intermediate.

The fact that the bromine and permanganate tests for unsaturation are negative and the IR indicates no peak at 3.40-$3.50\,\mu$ (existence of cyclohexenyl) also eliminates the unsaturated carbinol 3-(α, α, diphenyl methylol) cyclohexene $(C_6H_5)_2COH \cdot C_6H_9$ (m.w. 367). Although no tests were undertaken to prove the existence of two hydroxyl groups (the quantitative tests available are relevant only for water soluble alcohols), the saturated carbinol can be eliminated by its low melting point (α, α, diphenyl methylol) cyclohexane $(C_6H_5)COH \cdot C_6H_{11}$ (m.p. 73, m.w., 264).

This leaves only benzopinacol $(C_6H_5)_2COH \cdot COH \cdot (C_6H_5)_2$ (m.p. 182, m.w. 366) to be accounted for. The existence of this material must be considered for two reasons: First, the fact that isopropanol is the solvent includes the possibility of a competing reaction between benzophenone and isopropanol to produce the pinacol; second, the physical data, tertiary hydroxyl, no unsaturation, high molecular weight and melting point just as strongly indicate the possibility of benzopinacol. However, the periodic acid test for glycols was positive for a sample of benzopinacol and negative for the unknown. Even more conclusive is the fact that a mixed melting point of benzopinacol and the unknown showed a melting point depression of approximately 40°.

Therefore, by a process of elimination, the unknown has been shown to be none of the previously mentioned compounds. The fact that it is indeed the dicarbinol, 1, 2 bis (α-α diphenyl methylol) cyclohexane of molecular weight 456 tends to be supported by all the physical data. It explains the presence of a tertiary hydroxyl group, the absence of unsaturation, and the differential solubility (a two-dimensional model of the dicarbinol shows large blocking of the OH groups by the bulky phenyl groups. This would explain its insolubility in water, an inorganic polar solvent, and its solubility in acetone and ethyl acetate (both polar organic solvents). It corroborates the molecular weight estimation by the Cottrell apparatus (m.w. 400-500) although not that by the Rast method (at the moment this is unexplainable). Finally, with the elimination of benzopinacol, the per cent composition comes close to that predicted for the theoretical compound.

Several conclusions can be briefly drawn from this identification. First, steric hindrance by the phenyl groups does not prevent formation of the dicarbinol, thus extending the usefulness of deMayo's conclusions and disproving those of Heimlich (24). Second, even in the presence of isopropanol, the benzophenone-cyclohexene reaction tended to proceed to completion, indicating that not only did no competing reaction take place effectively but also that under photochemical conditions, an allelic hydrogen is still abstracted more easily than a secondary hydrogen (from isopropanol). However, it should be noted that there is a possibility of the benzopinacol being produced, provided that all the cyclohexene has reacted. The existence of very small amounts of benzopinacol might account for the discrepancy in per cent composition.

Turning now to sections III-VI and taking the recent findings involving isopropanol into account, the hypothesis predicts that in both cases the unsaturated carbinol should be produced. However, before attempting to interpret the data, the change in reaction conditions should be discussed.

In part I, the ultraviolet source was the sun and the reaction beaker was some type of pyrex glass. The radiation was of high intensity and saturated the entire surface area of the solution so that the reaction proceeded quickly and effectively. The pyrex glass, as mentioned, only permitted the entrance of radiation down to approximately 2800-3000°A and thus effectively allowed only absorption and subsequent reaction by the enervated ketone. In parts III-VI, on the other hand, the ultraviolet source was a mercury arc lamp of the same comparable intensity but of greatly diminished beam width. This not only necessitated a longer irradiation period but also reduced the number of molecules coming in contact with the radiation. In addition, the quartz glass was transparent to radiation of as low as 2000^{o}A. Considering that the double bond absorbs effectively from 1800-2800 A^{o} (30), there was the distinct possibility of a secondary enervation.

With these facts in mind, the data are more easily explainable. According to both deMayo (17) and Yang (16), reaction of a ketone with an olefin in an oxygen-free atmosphere yields both a carbinol and a hydrocarbon corresponding to a dimer of two of the original olefin molecules. For example, acetone and cyclohexene produce dimethyl cyclohexenyl carbinol and 3-3 biscyclohexenyl. Since the reaction of benzophenone and cyclohexene has proved that the theory holds for higher molecular weight diaryl ketones in the presence of oxygen, it is reasonable to expect that an analogous reaction will occur in the absence of oxygen. The products should therefore be diphenyl cyclohexenyl carbinol and 3-3 biscyclohexenyl. However, examination of the data from the reattions both with and without isopropanol as the solvent, indicate that it is not so.

In no case did an alcohol seem to have been produced. An examination of the infra-red spectra of the four stages of the cyclohexene-benzophenone separation shows no definite hydroxyl peak (in the 2.15-2.60 μ region). The only peak extant can be explained as a harmonic at 2.95 μ of the major peak at 5.9 μ . Further corroboration can be found in the fact that the xanthate test for alcohols gave negative results.

On the other hand, both the infra-red spectra and the μ-u spectra of the petroleum ether fraction do indicate the existence of an unsaturated bond in the product solution. The peak at 3.40-3.50μ in the infra-red corresponds closely to that found in the spectra of cyclohexene (not shown), while the shoulder at 230 mμ in the ultraviolet corresponds to a "submerged maxima appearing as an inflection or a bend and indicating a carbon-carbon double bond" (31). Further evidence can be found in the bromine and permanganate tests, both positive for unsaturation, and somewhat more unusually in the calcium hydride test for active hydrogen, which was positive for both the product and for a sample of pure cyclohexene (the allelic hydrogen probably being acid enough to react). Although not enough material remained for a molecular weight determinator or a per cent composition analysis, the high boiling point (90°C. at 40 mm.) definitely rules out cyclohexene, and the absence of a hydroxyl group eliminates the unsaturated alcohol. The material is therefore most probably the 3-3' biscyclohexenyl.

The methanol fraction contained the unreacted benzophenone. A major peak at 252 mμ and a minor one at 330 mμ in the ultraviolet corresponded exactly to those of a pure sample of benzophene (32).

The only conclusions that can be drawn from these two sets of data are: one, that in the absence of air, the biscyclohexenyl is the sole product and, two, that irradiation from outside the solution under these conditions is singularly ineffective in promoting carbinol formation. Since carbinols were produced by analogous ketones with the same olefin, and since previously discussed work did yield the more sterically hindered dicarbinol, the only outstanding reason for the lack of product must lie in some defect of the irradiation conditions.

The final reaction carried out was that of cyclohexene-benzophenone in direct sunlight. Although time limitations have prevented the completion of product identification, the data accumulated thus far have yielded fairly significant clues. An IR taken immediately upon completion of the reaction, as well as those taken later for the various eluant factions very strongly indicated the presence of a hydroxyl group by an absorption at 3520 cm^{-1} (2.85μ). This is corroborated by the xanthate test. Removal of the unreacted cyclohexene followed by bromine test for unsaturation in the remaining solutions just as strongly point to the existence of a carbon-carbon double bond, either in the alcohol or as part of 3-3' biscyclohexenyl.

At first glance these conclusions (parts VII and VIII) tend to belie those found for parts I and II. The reaction of cyclohexene and benzophenone in sunlight and under oxygen has produced what appears to be an unsaturated carbinol rather than the previously identified saturated dicarbinol. However, examination of laboratory procedures confirmed that the last preparation was previously de-oxygenated before being irradiated, so that what was thought to be an excess of oxygen was in fact an oxygen-free atmosphere. Under these conditions, the expected product would indeed be the unsaturated carbinol, 3-(α,α, diphenyl methylol) cyclohexene.

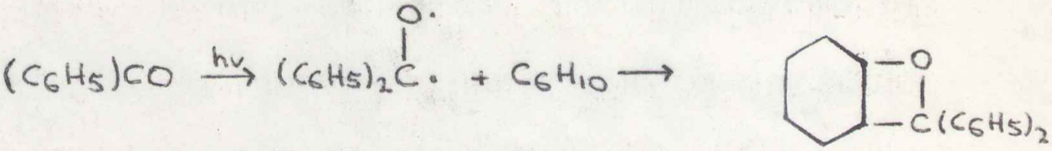
Not so easily explained, though, are the results obtained by Heimlich (24). Although he failed to completely substantiate his preliminary identification by a direct synthetic route, the melting point (m.p. 73°C.) and the infra-red spectrum almost positively identify the compound as (α,α, diphenyl methylol) cyclohexane (or diphenyl cyclohexyl carbinol). The existence of this particular compound, the saturated carbinol, is both without experimental or mechanistic precedent. Indeed, Heimlich also predicted, although by a different mechanism than that postulated by deMayo, the existence of the saturated dicarbinol. However, in view of his results, he suggested first the possibility of steric hindrance preventing formation of the dicarbinol, and second the abstraction of a hydrogen ion from the solvent (isopropanol) to produce the cyclohexylcarbinol.

Subsequent attempts under the same experimental conditions have repeatedly failed to produce the same material. The great disparity in melting points, that of the carbinol being 73°C., and that of the dicarbinol being 194°C, and in infra-red spectra completely precludes this. In fact, the existence of the dicarbinol refutes Heimlich's hypothesis that steric hindrance was the reason for carbinol formation.

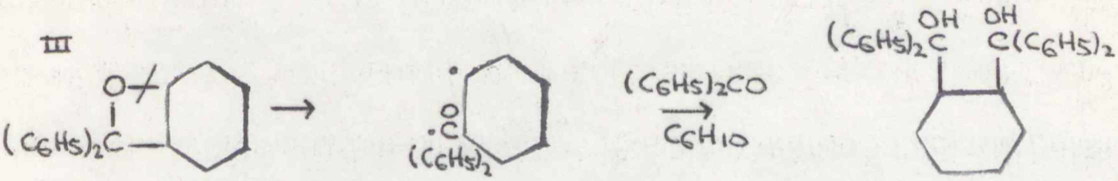
It also seems that, based on the large body of evidence concerning hydrogen abstraction by the activated ketone (11)(12)(13)(14)(15)(16), deMayo's own hypothesis for dicarbinol formation ought to be reconsidered. According to deMayo (20), the genesis of the dicarbinol did not involve the cyclohexenyl radical at all, the radical being trapped by the excess oxygen as cyclohexene hydroperoxide (I). He therefore proposed the formation of an oxetane intermediate, which by instability and cleavage became the dicarbinol.

I. $C_6H_9\cdot + O_2 \xrightarrow{C_6H_{10}} C_6H_9O_2H + C_6H_9\cdot$

II



III



However, this hypothesis seems unpractical for two reasons: First, using Occam's Razor, the entire mechanism is unnecessarily complicated. As will be seen, there is no need to incorporate the existence of an oxetane intermediate. Second, at no point does deMayo propose hydrogen abstraction, and, in view of the evidence, there is no reason why it should be used in all other mechanistic schemes and not in this one.

On the other hand, the auto-oxidation of benzaldehyde has been shown to proceed by a free-radical mechanism that is easily applicable (33). When hexaphenyl ethane and benzaldehyde are irradiated in the presence of oxygen, the hydrogen dissociates to free radicals and catalyzes the auto-oxidation.

$$(C_6H_5)_3CC(C_6H_5)_3 \rightarrow (C_6H_5)_3C.$$

$$(C_6H_5)_3C \cdot + O_2 \rightarrow (C_6H_5)_3COO \,.$$

$$(C_6H_5)_3COO \cdot + C_6H_5CHO \rightarrow (C_6H_5)_3CO_2H + C_6H_5CO \,.$$

$$C_6H_5CO_2 \cdot + O_2 \rightarrow C_6H_5COO_2 \cdot$$

$$C_6H_5COO_2 \cdot + C_6H_5CHO \rightarrow C_6H_5COO_2H + C_6H_5CO.$$

The oxygen molecule has two unpaired electrons and may thus be regarded as a sort of diradical. It is not a sufficiently reactive radical to attack most organic molecules but it will combine with free radicals.

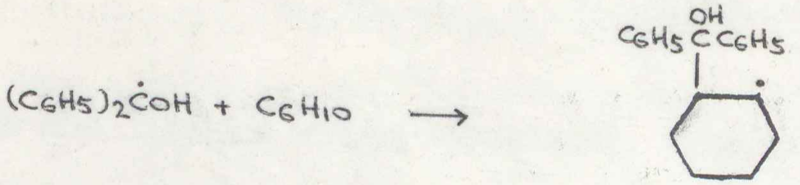
By incorporating both the above mechanism and hydrogen abstraction by the ketone, a new hypothesis may be proposed.

I $$(C_6H_5)_2CO \xrightarrow{h\nu} \left[(C_6H_5)_2CO\right]^*$$

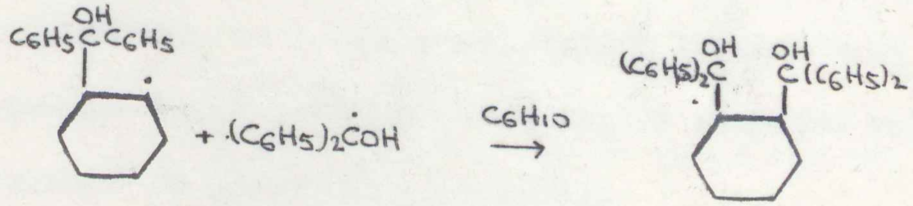
II $$\left[(C_6H_5)_2CO\right]^* + C_6H_{10} \longrightarrow (C_6H_5)_2\dot{C}OH + C_6H_9\cdot$$

III $$C_6H_9\cdot + O_2 \xrightarrow{C_6H_{10}} C_6H_9O_2H$$

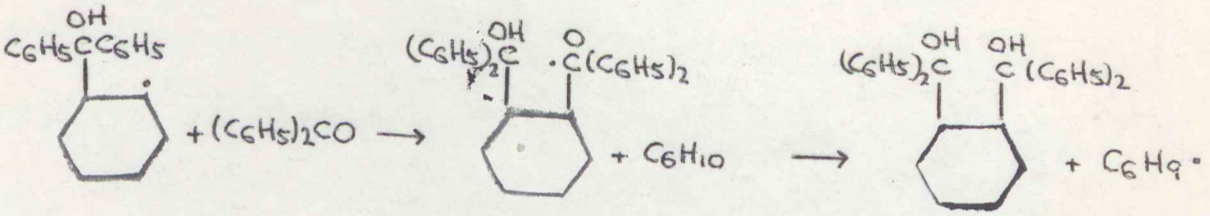
IV



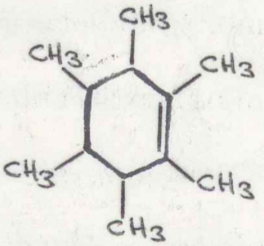
Ⅴa



or Ⅴb



The most serious objection lies in the ease with which side products may form from the various reactive species and interfere with formation of the main product. However, the existence of these compounds, such as the pinacol or unsaturated carbinol, even in small amounts would substantiate the mechanism. A more stable ring structure, such as



might also confirm either hypothesis, since the stability would tend to retain the oxetan intermediate and prevent its cleavage, or a more quantitative treatment of the mechanism might indicate a measurable reaction rate more dependent on one of the reactants.

SUMMARY

It has been the purpose of this thesis to

1. re-run Heimlich's experiment to determine if the cyclohexyl and not the cyclohexenyl carbinol has been produced. This experiment, the photochemical reaction of benzophenone, cyclohexene, and isopropanol, is described in part I of the Experimental Results section. The product, 1, 2-bis (α,α, diphenylmethylol) cyclohexane has been carefully identified by means of infra-red spectra and qualitative organic analysis. It has not been found to correspond to either the carbinol produced by Heimlich (α,α, diphenylmethylol) cyclohexane or to the unsaturated carbinol, 3-(α,α, diphenylmethylol) cyclohexene.

2. determine whether or not steric hindrance prevents deMayo's hypothesis from being extended to aryl ketones. The existence of the dicarbinol corroborates deMayo's findings on lower molecular weight ketones and seems to indicate that the hypothesis is valid for the entire ketone family. Steric hindrance, in the case of diaryl compounds, plays no part in determining the products,

and therefore refutes Heimlich's contention that it causes unsaturated carbinol formation.

3. determine if there is competition between secondary hydrogen abstraction from isopropanol and allelic hydrogen abstraction from cyclohexene. The production of the dicarbinol rather than the pinacol, even in the presence of isopropanol seems to indicate preferential abstraction of the allelic hydrogen over the secondary hydrogen. However, more definitive proof would await a change of mole ratios among the reactants.

In addition, other experiments have been run under ultraviolet light with the same reactants. These, on the whole, have been inconclusive, indicating only the presence of 3-3 biscyclohexenyl.

Finally, a new mechanism has been proposed for dicarbinol formation and several experiments have been suggested to confirm or deny it.

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