QUENCHING STUDIES ON THE PHOTOCHEMICAL REARRANGEMENT OF CYCLIC KETONES

THESIS FOR THE DEGREE OF M. S.
MICHIGAN STATE UNIVERSITY
ROGER WILLIAM SPOERKE
1969

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Peter Wagner
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Quenching Studies on the Photochemical Rearrangement of Cyclic Ketones

By

Roger Wm. Spoerke

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Lastly,it is my pleasure to thank my wife not only for her assistance in preparing this manuscript but also for her sympathetic encouragement during those early dark days when results were few and progress seemed negligible.

Abstract

Dienes were used to quench the photoisomerization of several cycloalkanones in dilute solution. Cyclopentanone and substituted cyclohexanones apparently undergo the photoisomeric reaction via the triplet excited state, in the liquid phase.

Rate constants were calculated for these various ketones in their triplet states: cyclopentanone, 1.1×10^{8} sec^{-1}; cyclohexanone, 3.3×10^{7}sec^{-1}; 2-methylcyclohexanone, 4.7×10^{8}sec^{-1}; 3-methylcyclohexanone, 2.5×10^{7} sec^{-1}; 3,5-dimethylcyclohexanone, 2.4×10^{7}sec^{-1}; 3,3,5-trimethylcyclohexanone, 2.5×10^{7}sec^{-1}; 2,6-dimethylcyclohexanone, 9.3×10^{8}sec^{-1}; 2-phenylcyclohexanone, 3.3×10^{8}sec^{-1}; 2,2-dimethylcyclohexanone, 1.8×10^{9}sec^{-1}.

Quantum yields for the disappearance of the ketones and quantum yields for the appearance of their respective triplet products were also determined: cyclopentanone, $\phi_{-k}= .27$, $\phi_{+p}= .24$; cyclohexanone, $\phi_{-k}=.13$, $\phi_{+p}= .09$; 2-methylcyclohexanone, $\phi_{-k}= .50$, $\phi_{+p}= .42$; 3-methylcyclohexanone, $\phi_{-k}= .08$, $\phi_{+p}= .03$; 3,5-dimethylcyclohexanone, $\phi_{-k}= .03$, $\phi_{+p}= .005$; 2,6-dimethylcyclohexanone, $\phi_{-k}= .56$, $\phi_{+p}= .40$; 3,3,5-trimethylcyclohexanone, $\phi_{-k}= .02$, $\phi_{+p}= .002$; 2-phenylcyclohexanone,

$\not{0}_{-k}= .51$, $\not{0}_{+p}= .04$; 2,2-dimethylcyclohexanone, $\not{0}_{-k}= .54$, $\not{0}_{+p}= .42$.

It is proposed that reactivities of n,π^* carbonyl triplets are dependant on ring size and substitution on the ring.

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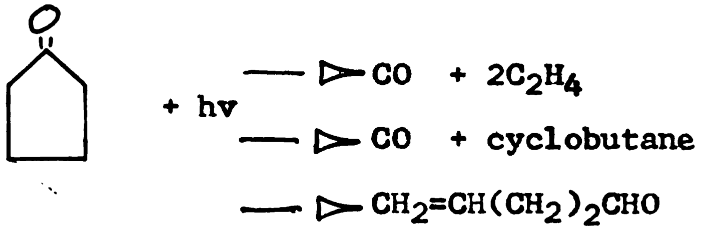
Introduction

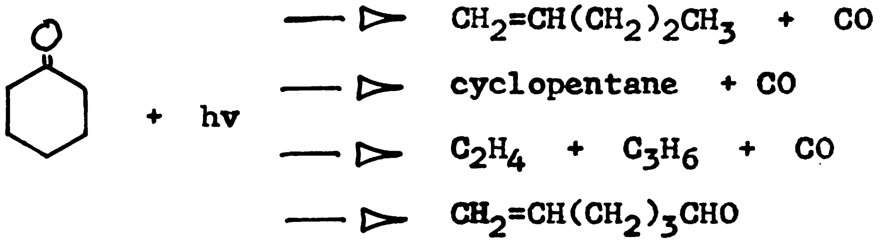
Cyclic five- and six-membered ring ketones undergo photoisomerizations which involve cleavage of the bond between the carbonyl and the alpha carbon (1). The same type of phenomenon can be observed in the alkoxy free radical system (2). The weak absorption band at 280-360mμ, noted in ketones, arises from the n,π^* transition (3). The breakage of that bond involves a non-bonding electron on oxygen being promoted to an antibonding pi orbital. The alkoxy radical system should serve as a good model for the n,π^* triplet state, since both species possess an electron deficient oxygen atom. This statement has been validated by comparing relative reactivities of hydrocarbons toward both the n,π^* triplet states of ketones and tertiary butoxy radicals. Relative reactivities of hydrocarbons depend on the C-H bond strength in the same fashion toward both abstracting species (4).

The photolysis of cyclopentanone in the vapor phase has been the subject of several investigations over the past 25 years (5-8). It was shown by Benson and Kistiakowsky (9) that the products of its photolysis are carbon monoxide, ethylene and cyclobutane. Later work (7) then showed 4-pentenal to be an important product also. From the consideration of the mass balance relationships, three photochemical processes were proposed.



It was concluded the products were formed from the excited singlet state (10).

Cyclohexanone was then studied in the vapor phase also (11). Photolysis of cyclohexanone yielded products such as carbon monoxide, ethylene, propylene, cyclopentane, pentene and 5-hexenal.

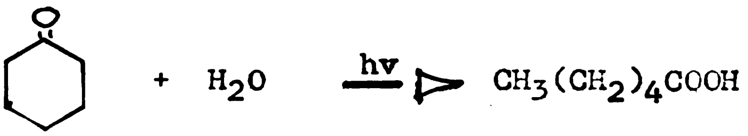


With both ketones, the hydrocarbons and the unsaturated aldehydes were not totally quenched by the addition of oxygen (12). It was concluded the primary photochemical processes of cyclopentanone and cyclohexanone are very similar in the gaseous state, in that the reaction is occuring primarily from the excited singlet state.

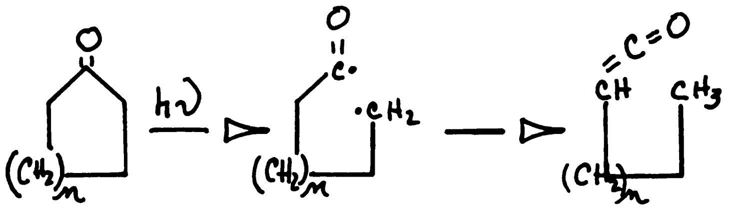
Until recently, the photochemistry of the cyclic ketones in the condensed phase has not been throughly examined. There are several factors which would cause a difference between vapor and liquid phase photolysis. In the liquid state, there is much more association between nearest neighbor molecules; therefore, there would be many more collisions between molecules than in the gaseous state where the molecules are more dispersed. With more of these collisions occuring, whether it be between two ketone molecules or between a ketone and a solvent molecule, there would be a rapid loss of vibrational energy in the electronically excited ketone molecule. Another factor to be considered is the possibility of chemical reaction between the excited ketone molecule and a solvent molecule. Finally, it has been observed (13,14) in the condensed phase that cyclopentanone shows evidence for the existence of triplet state molecules, which were not observed by Srinivasan in the gaseous phase (15). The facts mentioned here show the need for careful quantitative experimentation to be made on the liquid phase reactions of cyclic ketones.

Pitts and co-workers (16) have recently performed such determinations on cyclopentanone and cyclohexanone. They reported triplet lifetimes of $.04 \times 10^{-7}$sec and $.83 \times 10^{-7}$sec for cyclopentanone and cyclohexanone, respectively.

The photolysis of cyclohexanone has been well studied in the liquid phase by several workers, and formation of 5-hexenal, presumably by an intramolecular rearrangement, was found to be the major product (17). The formation of 5-hexenal is capable of being quenched, while formation of 2-methylcyclopentanone, another product, is not. This suggests that these two products occur from two different excited states of cyclohexanone; 5-hexenal from the triplet state and the unquenchable 2-methylcyclopentanone from the singlet state (17). Cyclohexanone behaves similarly in 1-octene solution to yield quenchable 5-hexenal, and unquenchable 2-methylcyclopentanone (18). When cyclohexanone is photolyzed in aqueous solution, a reaction has been observed(19,20) which leads to the formation of caproic acid, the total reaction being the addition of one molecule of water and the cleavage of the ring ketone.

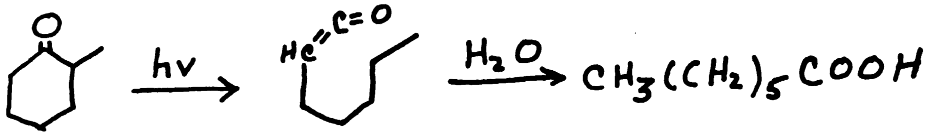


During recent investigations by Yates (21) on cyclic ketones of the form $\overline{CH_2CH_2(CH_2)_nCH_2C}O$, it was found that a ketene is produced as a major isomeric product:

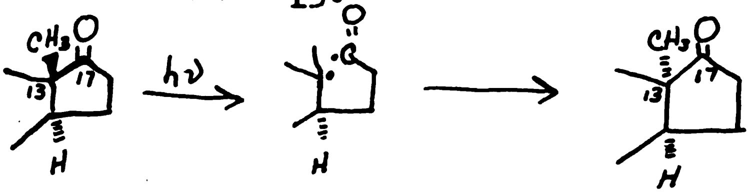


Quinkert (22) has related the difficulty of ketene formation in the case of cyclopentanones relative to cyclohexanones.

Cyclopentanone (17), dihydrocarvone (23), menthone (24), and 2-methylcyclohexanone (25) also undergo a reaction to yield an unsaturated aldehyde. In an aqueous alcoholic solution, 2-methylcyclohexanone and menthone undergo a light induced hydrolysis to form the open chain acid as shown here (24):

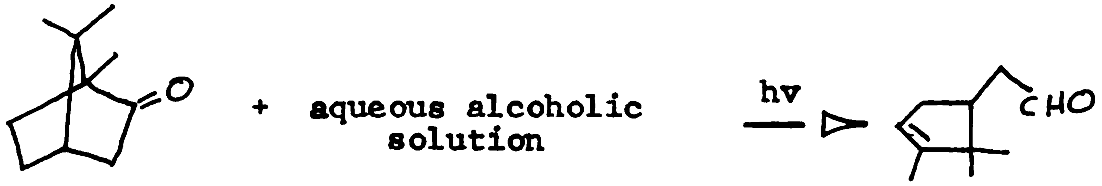


It is generally assumed that in the condensed phase, the photolytic dissociation of acyclic ketones is retarded by collision deactivation(26) and that the radicals formed are removed, at least in part, because of the cage effect postulated by Franck and Rabinowitch (27). If the rate of recombination of the radicals produced is not faster than the rate with which the alkyl radical center loses its original disymmetry, racemization should then occur in a ketone which has an assymetric alpha carbon. In the early forties, Butenandt and co-workers (28) found that 17-Ketosteroids suffer a partial photo-epimerization at C_{13}.



Since then, many cases of this type of behavior have been observed (29,30,31).

Other investigations have shown that camphor photolyzed in aqueous alcoholic solution (32) leads to alpha-campholenic aldehyde as the major product.

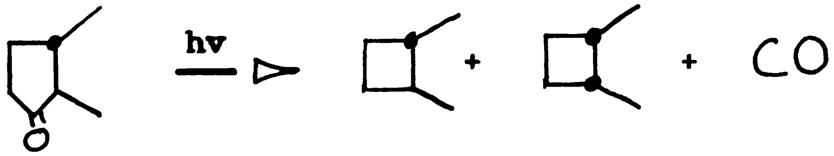


This photoreaction of camphor is analogous to alkenal formation from monocyclic five- and six-membered ketones.

Many authors have proposed theories to account for these photochemical transformations (33,34,35,36). Srinivasan originally reported that 2-methylcyclohexanone gave only trans-5-heptenal (36), in conjunction with his postulated concerted mechanism, to yet be described. Alumbaugh and co-workers (37) have since reported that 2,6-dimethylcyclohexanone yields both cis- and trans-2-methyl-5-heptenal in the same ratio independant of the starting materials geometry.

Recently, Pritchard and co-workers (38) have re-examined 2-methylcyclohexanone and proved the products of photolysis to be both the cis- and trans- aldehydes. In keeping with the relative thermodynamic stabilities of secondary versus primary radicals (39), the preference of the 1,2 bond cleaving rather than the 1,6 bond, is more than 50 times greater for the former.

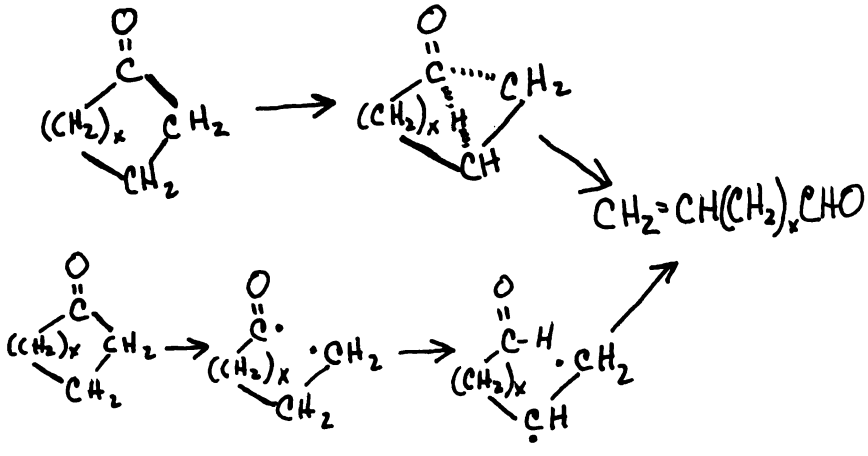
Frey (40) has investigated the photochemical decomposition of trans- 2,3-dimethylcyclopentanone and noted products of cis and trans 1,2-dimethylcyclobutane. Since both were formed, it seems that a biradical intermediate is necessary to account for them.



The two mechanisms which have been postulated to account for the behavior of acyclic ketones are described here. One involves a concerted type rearrangement (36,41) as shown in Equation Scheme 1, and the other postulates a biradical intermediate (42) as indicated in Equation Scheme 2. Both postulated mechanisms account for the observed aldehydic product.

Equation Scheme 1

Equation Scheme 2



There are at least four points to give support to the biradical mechanism. It is known that ketones do undergo the alpha type cleavage, both aliphatic and alicyclic (43,44,45,46,47). The racemization of the 17-ketosteroids could only occur if the alpha bond became ruptured to allow rotation about the C_{13} bond and thus lose its assymetry. If a concerted type mechanism were operative, the C_{13} centre would remain intact. The biradical mechanism also allows 2,6-dimethylcyclohexanone to yield equal amounts of cis and trans alkenal, independant of the geometry of the starting ketone; The quenchability of the observed products by oxygen or dienes points to an intermediate involving unpaired spins, which strongly suggests a 2-step mechanism.

The method employed in this investigation is the quenching of the triplet product by a diene; a method used and explained by many workers (48,49). Dunion and Trumbore (50) have shown that most of the observed isomerization of the cyclic ketones can be quenched by suitable triplet quenchers. This fact allows us to quantitatively study the photoisomerization of the cyclic ketones. The schematic representation of the process is shown here:

$$K^{o} + hv \longrightarrow K^{1*}$$

$$K^{1*} \xrightarrow{i.c.} K^{3*}$$

$$K^{3*} + \text{Diene} \xrightarrow{k_q} K^{o} + \text{Diene}^{3*}$$

$$K^{3*} \xrightarrow{k_r} \text{Products}$$

$$K^{3*} \xrightarrow{k_d} K^{o}$$

By the application of steady state approximation, the Stern-Volmer equation correlates these values into a usable form:

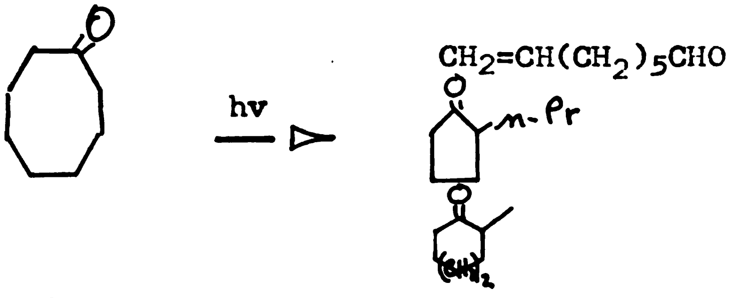
$$\phi_o / \phi_a = 1 + k_q \tau [Q] \qquad \frac{1}{\tau} = k_r + k_d$$

where ϕ_o is the quantum yield for the formation of aldehyde in the absence of quencher and ϕ_a is the quantum yield for formation in the presence of a quencher, i.e. a diene. A linear plot occurs when the ratio ϕ_o / ϕ_a vs. [Quencher] is made; this presupposes the aldehyde is formed only from the triplet state. The slope of this plot is then equal to $k_q \tau$. The bimolecular quenching constant in the solvent benzene has been calculated to be 5.0×10^9 liter/mole sec (51). The lifetime of the triplet state can then be found. Piperylene was used as a quencher, in most cases, since it is a very efficient acceptor of the triplet energy of ketone triplets, but does not quench their singlet states (52).

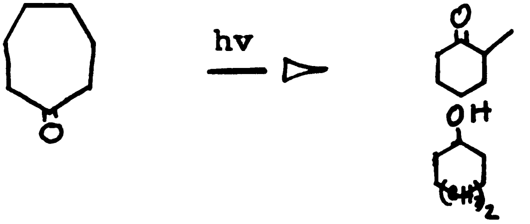
This particular investigation was involved mainly with C_5 and C_6 cyclic ketones, but a discussion about them would not be complete without mentioning results of experimentation on their C_4, C_7, and C_8 analogs. Cyclobutanone has been studied by several workers (53,54) and quantum yields for products obtained were calculated. The yield of C_3H_6 was found to increase with decreasing cyclobutanone pressure and with shorter wavelengths, while the yield of c-C_3H_6 was unaffected. A mechanism involving formation of C_3H_6 from an excited triplet cyclobutanone, possibly involving a diradical intermediate, has been proposed.

$$K + h\nu \longrightarrow {}^{1}K$$
$${}^{1}K \longrightarrow c\text{-}C_3H_6 + CO$$
$${}^{1}K \longrightarrow C_2H_4 + CH_2CO$$
$${}^{1}K \xrightarrow{i.c.} {}^{3}K$$
$${}^{3}K \longrightarrow \cdot CH_2CH_2CH_2\cdot + CO$$
$$\cdot CH_2CH_2CH_2\cdot \longrightarrow CH_3CHCH_2$$
$${}^{3}K + M \longrightarrow K + M$$

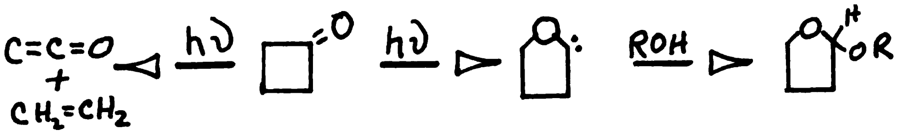
Bernard (55) and Srinivasan (25) made an investigation on cyclooctanone, and noted that photolysis in cyclohexane solution yielded reduction products of cyclooctanol and an unidentified bicyclooctanol. In the pure liquid phase, a mixture of products were observed:



Srinivasan (56,25) also studied the photolysis of the cycloheptanone system and found it to decompose yielding a similar array of products.



Turro and Southam (57) also studied cyclobutanone in methanol and found that ring expanded cyclic acetals were formed. This work shows an intermediate biradical leading to carbene formation.



The investigation presented here was begun to examine various cycloalkanones, and to determine how ring size and substitution on them affects the photochemistry of the triplet states. The effects of this substitution on the quantum yields was also studied. The systems that were chosen to accomplish this effort are cyclopentanone and various methyl and phenyl substituted cyclohexanones. The available information on the photochemistry of substituted cyclopentanones and cyclohexanones indicates that the presence of one or more alkyl substituents on the ring does not lead to any new photochemical reactions; but as this paper shows it does effect rate of reaction and quantum yields for various products. It is hoped that through this study, the photoreactivity of cyclic ketones may be better understood.

Results

It has been discussed in the introduction how the Stern-Volmer equation is applied and what results can be derived from it. The importance of quenching studies on these ketones is essential, since very little is known about the relationship between triplet state reaction rates and molecular structure. The quantum yield for these triplet state reactions are also important.

I. Quenching Studies

A degassed solution of each ketone in benzene was irradiated at 3130 Å. Vapor phase chromatograph traces of the irradiated samples are displayed in Figures 16-22. In most cases, the major product peak appears at approximately one-half the retention time of the parent cyclic ketone. In the presence of quencher, the area of the major product peak is reduced. That this peak corresponds to the aldehyde was established by adding some authentic aldehyde to the irradiated sample and observing an increase in area of the major product peak. The major products of some of the ketones 4-pentenal, 5-hexenal, and 2-methyl-5-heptenal were prepared by irradiation of cyclopentanone, cyclohexanone, and 2,6-dimethylcyclohexanone in benzene, respectively. These products were isolated by preparative vapor phase chromatography. Comparison of their infra-red spectra to those presented by Srinivasan, and appearance of aldehydic and vinyl protons in their NMR spectra, were deemed sufficient for their identification. It was assumed that the analogous vpc product peak for the other ketones corresponded to the expected ω-alkenals. In all cases, the pungent odor associated with an aldehyde was easily detected. Other unidentified peaks were observed to be formed in low yields for all ketones studied.

Quenching studies were performed by irradiation of 0.1-0.2 M cyclic ketones at 3130 Å in degassed benzene solution containing a known concentration of an internal standard and various known concentrations of quencher, either piperylene or 2,5-dimethyl-2,4-hexadiene. Relative quantum yields of ω-alkenal were found at low conversion and of ketone disappearance at high conversions. The slopes of the Stern-Volmer plots, together with triplet lifetimes calculated from them, are contained in Tables I-XII. Details for each study are in the experimental section of this thesis. For each ketone, almost all ω-alkenal formed could be quenched by high concentrations of piperylene or 2,5-dimethyl-2,4-hexadiene; however, not all ketone disappearance could be quenched due to small amount of singlet reaction occuring.

A. Cyclopentanone

Table I.

Effect of Quenching on Cyclopentanone

[Ketone]	Time Irradiated	% Reacted	Slope(M^{-1})[a]	τ(sec)	$\frac{1}{\tau}$(sec^{-1})
.2 M	68 hrs.	54 %	21	4.2×10^{-9}	2.4×10^{8}
.1 M	6 hrs.	11 %	46	9.3×10^{-9}	1.1×10^{8}
.1 M	5½ hrs.	10.2 %	48.4	9.7×10^{-9}	1.1×10^{8}

[a] Value equal to $k_q\tau$ and calculated from slope of Stern-Volmer plot.

B. Cyclohexanone

Table II.

Effect of Quenching on Cyclohexanone

Ketone	Time Irradiated	% Reacted	Slope(M^{-1})[a]	τ (sec)	$\frac{1}{\tau}$(sec^{-1})
.2 M	90 hrs.	43 %	292	8.3×10^{-8}	1.2×10^{7}
.1 M	10 hrs.	14 %	147	2.9×10^{-8}	3.4×10^{7}
.1 M	9½ hrs.	12 %	155	3.1×10^{-8}	3.2×10^{7}
.1 M	9 hrs.	10.2 %	151	3.0×10^{-8}	3.3×10^{7}

[a] Value given is equal to $k_q\tau$ and was found using Stern-Volmer plot.

C. 2-Methylcyclohexanone

Table III.

Effect of Quenching on 2-methylcyclohexanone

Ketone	Time Irradiated	% Reacted	Slope(M^{-1})[a]	τ (sec)	$\frac{1}{\tau}$(sec^{-1})
.2 M	75 hrs.	77 %	6.3	1.2×10^{-9}	8.0×10^{8}
.1 M	6 hrs.	14 %	10.9	2.2×10^{-9}	4.6×10^{8}
.1 M	9 hrs.	18 %	10.3	2.1×10^{-9}	4.8×10^{8}

[a] Value equal to $k_q\tau$.

D. 3-Methylcyclohexanone

Table IV.

Effect of Quenching on 3-Methylcyclohexanone

Ketone	Time Irradiated	% Reacted	Slope(M^{-1})[a]	τ (sec)	$\frac{1}{\tau}$(sec^{-1})
.2 M	114 hrs.	42 %	137	2.8×10^{-8}	3.6×10^{7}
.2 M	93 hrs.	26 %	240	4.8×10^{-8}	2.1×10^{7}
.1 M	12 hrs.	11 %	209	4.0×10^{-8}	2.5×10^{7}

[a] Value given equal to $k_q\tau$ and found using Stern-Volmer plot.

E. 3,5-Dimethylcyclohexanone

Table V.

Effect of Quenching on 3,5-Dimethylcyclohexanone

Ketone	Time Irradiated	% Reacted	Slope(M^{-1})[a]	τ(sec)	$\frac{1}{\tau}$(sec^{-1})
.1 M	22 hrs.	10 %	206	4.1×10^{-8}	2.4×10^{7}

[a] Value equal to $k_q\tau$ and calculated from slope of Stern-Volmer plot.

F. 3,3,5-Trimethylcyclohexanone

Table VI.

Effect of Quenching on 3,3,5-Trimethylcyclohexanone

Ketone	Time Irradiated	% Reacted	Slope(M^{-1})[a]	τ(sec)	$\frac{1}{\tau}$(sec^{-1})
.1 M	40 hrs.	10 %	199	4.0×10^{-8}	2.5×10^{7}

[a] Value equal to $k_q\tau$ and calculated from slope of Stern-Volmer plot.

G. 2,6-Dimethylcyclohexanone

Table VII.

Effect of Quenching on 2,6-Dimethylcyclohexanone

Ketone	Time Irradiated	% Reacted	Slope(M^{-1})[a]	τ(sec)	$\frac{1}{\tau}$(sec^{-1})
.1 M	4 hrs.	9 %	5.37	1.1×10^{-9}	9.3×10^{8}

[a] Value equal to $k_q\tau$ and calculated from Stern-Volmer plot.

H. 2-Phenylcyclohexanone

This particular ketone did not give the aldehyde as the major product, because the major peak observed could not be reduced when concentrations of 1M piperylene were used. The peak representing the aldehyde was located in a manner already described.

Table VIII.

Effect of Quenching on 2-Phenylcyclohexanone

Ketone	Time Irradiated	% Reacted	Slope(M^{-1})[a]	τ(sec)	$\frac{1}{\tau}$(sec^{-1})
.1 M	3 hrs.	10 %	15.2	3.0×10^{-9}	3.3×10^{8}

[a] Value equal to $k_q\tau$ and found using the Stern-Volmer plot.

I. 2,2-Dimethylcyclohexanone

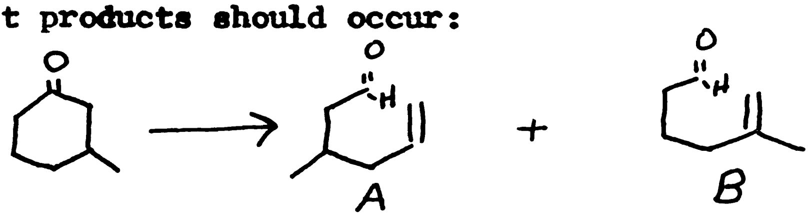
Table IX.

Effect of Quenching on 2,2-Dimethylcyclohexanone

Ketone	Time Irradiated	% Reacted	Slope(M^{-1})[a]	τ(sec)	$\frac{1}{\tau}$(sec^{-1})
.1 M	2 hrs.	8.2 %	2.79	5.6×10^{-10}	1.8×10^{9}

[a] Value equal to $k_q\tau$ and found using Stern-Volmer plot.

Special consideration was given to 3-methylcyclohexanone. When this molecule absorbs light, it seems two triplet products should occur:



Twenty-five grams of this ketone were diluted in benzene and then photolyzed. The major product was isolated and its NMR did not show the presence of allylic methyl. Srinivasan (58) originally reported the absence of the "B" isomer, which is in agreement with the results of this author.

II. Quantum Yield Determinations

Quantum yield studies were performed by irradiation of 0.1-0.2 M ketone at 3130 Å in degassed benzene solution containing a known concentration of an internal standard. An actinometer solution was used to determine the intensity of the light. The actinometer tubes consisted of 0.1-0.2 M cis-piperylene and a known amount of acetone in a degassed hexane solution. The quantum yield of sensitized cis- to trans-piperylene isomerization was taken to equal 0.56 (59).

The irradiated ketones were analyzed by vpc for product concentration and ketone concentration. The actinometer solutions were analyzed for conversions of cis to trans-piperylene. From this information, can be calculated the absolute quantum yields for product appearance and ketone disappearance can be calculated. Those values which were found for ketone disappearance are tabulated in Tables X and XI.

The quantum yield for disappearance of the cyclic ketone would be insignificant toward describing reaction pathways by which the parent ketone can be converted to aldehydic product. To give meaning to the values, the quantum yield for product appearance are given in Table XII.

It was noted, as the length of irradiation time increased, the value for quantum yields of product appearance decreased. To determine the cause of this observation, two sets of experiments were performed. One consisted of isolating various aldehydic products and obtaining their absorbance at a given concentration. The absorbances for parent ketones were also obtained, and then compared. A second experiment consisted of irradiating samples of both cyclopentanone and cyclohexanone with an internal standard in a degassed benzene solution, and analyzed for ketone and product concentrations at given time intervals. The graphic representation of data in Table XIV can be cited in Figures 14 & 15 .

A comprehensive table of data obtained in this investigation is given in Table XV.

TABLE X

RELATIVE QUANTUM YIELDS FOR DISAPPEARANCE OF KETONE AT HIGH CONVERSION

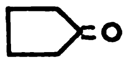
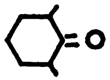
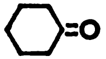
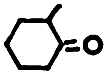
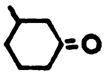
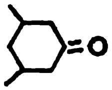
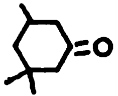
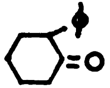
KETONE	% CONVERSION	RELATIVE Φ
	62	.52
	61	1.00
	28	.23
	64	.92
	21	.16
	11.6	.09
	7	.06
	51	.83

Table XI

Quantum Yields for Disappearance of Ketone at Low Conversion

Ketone	%Conversion	Relative ϕ_{-k}	Absolute ϕ_{-k}
2,6-dimethylcyclohexanone	21 %	1.00	.56
cyclopentanone	24 %	.50	.28
cyclohexanone	13.6 %	.23	.13
2-methylcyclohexanone	18 %	.89	.50
3-methylcyclohexanone	15 %	.14	.08
3,5-dimethylcyclohexanone	12 %	.059	.033
3,3,5-trimethylcyclohexanone	8.3 %	.043	.024
2-phenylcyclohexanone	22.4 %	.91	.51
2,2-dimethylcyclohexanone	22 %	.95	.54

Table XII

Quantum Yields for Product Formation

Ketone	Photo. Time	%Conversion	[Product]	[Prod]/hr	ϕ_{+p}
cyclopentanone	3 hrs.	9.5%	.0092M	.00307M	.24
cyclohexanone	2 hrs.	5.4%	.0021M	.00105M	.09
2-methylcyclohexanone	1 hr.	6.4%	.0050M	.00501M	.42
3-methylcyclohexanone	4 hrs.	6.2%	.0016M	.00034M	.034
3,5-dimethylcyclohexanone	12½hrs.	5.7%	.0008M	.00007M	.005
2,6-dimethylcyclohexanone	1 hr.	6.1%	.0048M	.0048M	.40
3,3,5-trimethylcyclohexanone	12½hrs.	2.7%	.0003M	.00002M	.0017
2-phenylcyclohexanone	1 hr.	13%	.0005M	.00052M	.04
2,2-dimethylcyclohexanone	2 hrs.	8.2%	.0096M	.00478M	.42

Table XIII.

Absorbances of Ketones and Their Products at 3130 Å

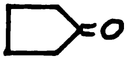
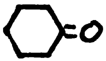
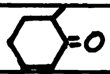
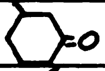
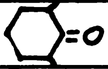
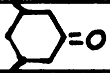
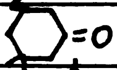
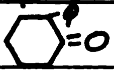
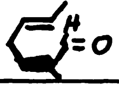
Substrate	Concentration	Wavelength	Absorbance	ε
	.1031 M	3130 Å	1.40	13.6
	.1113 M	3130 Å	.92	8.3
	.1180 M	3130 Å	1.10	9.3
	.0575 M	3130 Å	.468	8.2
	.1187 M	3130 Å	1.10	9.3
	.1031 M	3130 Å	.87	8.4
	.1090 M	3130 Å	.95	8.7
	.1358 M	3130 Å	1.98	14.6
	.2010 M	3130 Å	2.896	14.5
	.2000 M	3130 Å	2.713	13.6

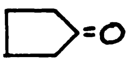
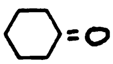
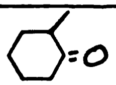
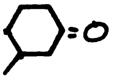
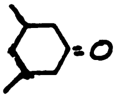
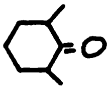
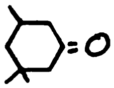
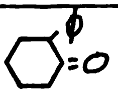
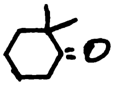
Table XIV.

Effect of Photolysis Time on Cyclopentanone and Cyclohexanone

Ketone	Photolysis Time	Ketone	Product
	0 hrs.	0.1158M	0.0000M
	3.0 hrs.	0.1054M	0.0092M
	8.5 hrs.	0.0843M	0.0224M
	14.0 hrs.	0.0680M	0.0322M
	26.0 hrs.	0.0497M	0.0445M
	0 hrs.	0.1110M	0.0000M
	3.0 hrs.	0.1005M	0.0032M
	8.5 hrs.	0.0930M	0.0044M
	14.0 hrs.	0.0880M	0.0043M
	26.0 hrs.	0.0780M	0.0036M

Table XV

Comprehensive Data of Quantum Yields
and Reaction Rates from Low Conversion Data

Ketone	ϕ_{-k}	ϕ_{+p}	$1/\tau$ (for -k)	$1/\tau$ (for +p)
	.27	.24	$2.4 \times 10^{8} sec^{-1}$	$1.1 \times 10^{8} sec^{-1}$ [a]
	.13	.09	$1.2 \times 10^{7} sec^{-1}$	$3.3 \times 10^{7} sec^{-1}$ [b]
	.50	.42	$8.0 \times 10^{8} sec^{-1}$	$4.7 \times 10^{8} sec^{-1}$ [c]
	.08	.03	-------	$2.5 \times 10^{7} sec^{-1}$
	.03	.005	-------	$2.4 \times 10^{7} sec^{-1}$
	.56	.40	-------	$9.3 \times 10^{8} sec^{-1}$
	.02	.002	-------	$2.5 \times 10^{7} sec^{-1}$
	.51	.04	-------	$3.3 \times 10^{8} sec^{-1}$
	.54	.42	-------	$1.8 \times 10^{9} sec^{-1}$

[a] Average of two values

[b] Average of three values

[c] Average of two values

Discussion

It seems evident from observing all of the data presented, that there are several phenomenon that need to be explained: 1) the effect of substitution on the alpha carbon, 2) the effect of beta carbon substitution, 3) effect of ring strain, 4) competitive absorption of the unsaturated aldehydes with their parent ketone.

When a ketone molecule absorbs a quantum of energy, a n electron is promoted to a pi^* state. The excited singlet rapidly crosses over to the triplet state ketone molecule. Various reactions can then occur from this excited state. The equilibriums involved depend on the size of the ring and the degree of substitution at the alpha carbon.

When molecular models of cyclopentanone and cyclohexanone are compared, the ring strain in cyclopentanone is obvious. The rate data shows the effect of this ring strain, with cyclopentanone 3 times more reactive than cyclohexanone. The enhanced reactivity can be attributed to the relief of ring strain when the molecule goes to the acyclic biradical.

The recoupling reaction can have a pronounced effect on the quantum yield of a reaction. Depending on how much recoupling competes with furthur reactions,the observed quantum yield will naturally be smaller than the true quantum yield with which the excited state reacts.

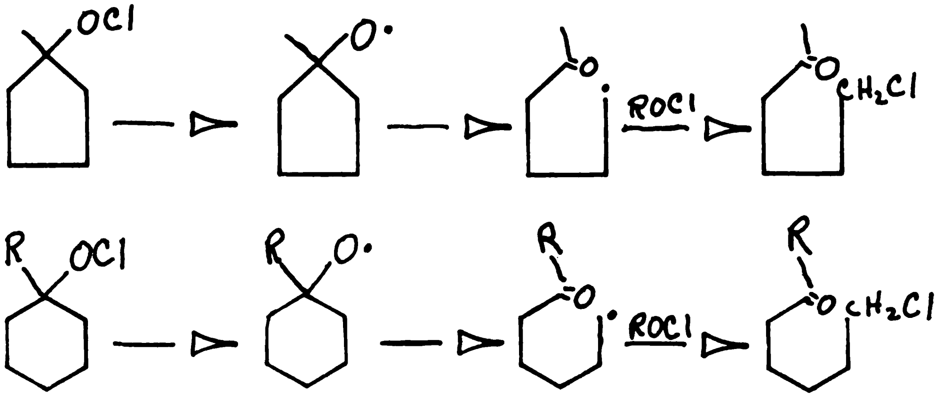
The degree of substitution at the alpha carbon is important in determining the triplet state reactivity. It is known that a tertiary free radical is more stable than a secondary or primary. This stabilization of free radicals can be considered the driving force of the reaction. Observation showed the formation of triplet product from cyclohexanone was less than that obtained from cyclopentanone, indicating that recoupling and ketene formation occur better in the 1,6 biradical. The observed quantum yield for 2-methylcyclohexanone is larger than cyclopentanone or cyclohexanone, and 2,2-dimethylcyclohexanone is larger than all of the ketones studied. Substitution on the alpha carbon also plays an important role in determining how long lived the excited state will be. The fact that the rate of reaction of the triplet 2,6-dimethylcyclohexanone is twice as fast as the rate for 2-methylcyclohexanone, can be attributed to the degree of alpha substitution. This correlation can be followed through all alpha substituted ketones studied;

i.e. 2-methylcyclohexanone is 15x faster than cyclohexanone, and 2,2-dimethylcyclohexanone is twice as fast as 2,6-dimethylcyclohexanone.

The effects of alpha substitution on reaction rate are summarized in the following table.

Ketone	Relative Rates
Cyclohexanone	1.0
2-methylcyclohexanone	14.3
2,6-dimethylcyclohexanone	28.0
2,2-dimethylcyclohexanone	54.2
2-phenylcyclohexanone	10.0

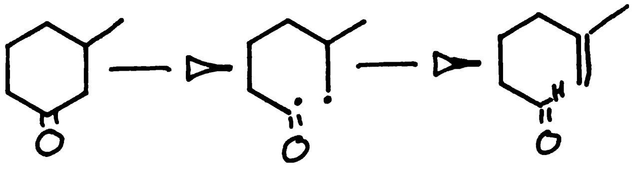
Many workers (60,61,62,63) have studied rates of H abstraction in cyclic ketones. In using alicyclic t-hypochlorites, the rate of this hydrogen abstraction by alkoxy radicals occurs in the order primary < secondary < tertiary. In the following sequence of reactions, it was found that the C_5 reacts faster than the C_6.



Alkyl groups are lost from tertiary alkoxy radicals in the sequence Me<<Et<i-Pr<t-Bu.

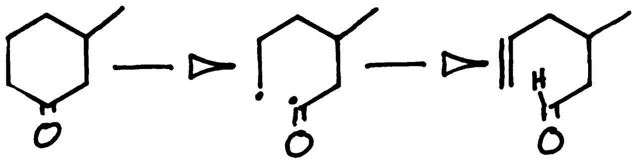
Substitution at the beta position does not affect the rate of cleavage nor the lifetime of the triplet. A reasonable assumption can be made that the cleavage rate for cyclohexanone, 3-methylcyclohexanone, 3,5-dimethylcyclohexanone, and 3,3,5-trimethylcyclohexanone should be comparable, as indeed the triplet lifetimes are. The quantum yield for triplet reaction, on the other hand, shows a marked dependance on beta substitution. When a ketone molecule cleaves to give the diradical, the positions of the orbitals on the carbonyl carbon and the beta carbon hydrogens must be properly aligned to allow hydrogen abstraction to occur. As the number of these beta hydrogens decrease, the probability that the preferred alignment for abstraction to occur decreases markedly. When triplet cyclohexanone cleaves, there are two beta carbons which can be abstracted, and two other hydrogens at the other beta carbon if the ring should open in that direction. This difference in cleavage cannot be detected without labelling the beta carbon with deuterium, so there are essentially fours hydrogens available for abstraction. In 3-methylcyclohexanone, however, the major triplet product is resultant from the fact that when cleavage occurs on the side containing the methyl group (Reaction A) the number of abstractable hydrogens has been reduced to one-half those available in cyclohexanone. If the preferred alignment is not obtained fast enough, either re-coupling or ketene formation may occur, reducing the quantum yield of the aldehyde.

Reaction A



If,on the other hand, cleavage occurs on the opposite side of the methyl group (Reaction B) than as in cyclohexanone two hydrogens are susceptible to abstraction and the probability of product formation is normal, leading to 3-methyl-5-hexenal as the major product rather than 5-methyl-5-hexenal.

Reaction B

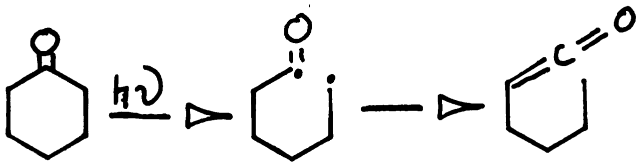


This observation would account for the quantum yield of product formation being about one-half that of cyclohexanone.

In 3,5-dimethylcyclohexanone and 3,3,5-trimethylcyclohexanone the number of abstractable hydrogens is reduced even more and hence a notable decrease in quantum yield for the formation of their respective triplet products.

During this investigation, it was observed repeatedly that quantum yield values were subject to change depending on length of irradiation time. It has been suggested that as the concentration of the aldehydic product builds up in the solution, the reaction to produce more product is suppressed, presumably by the unsaturated aldehyde itself, as well as by the ketene by-product. From the analysis of the data shown in Table XIII&XIV, and that in Figures 14&15 , it is postulated that the aldehyde acts more as an "internal filter" rather than as a quencher. The aldehydic products, in most cases, absorbs light as strongly as their parent ketone as shown by absorbance data, given in the results section.

In a recent paper by Yates (64), it was concluded that a major product of cyclohexanone photolysis is the ketene.



This reaction was discussed briefly in the introduction, but a conclusion can be made from this observation. When ketones are chosen carefully, the formation of aldehydic products can be hindered; e.g. 3,3,5,5-tetramethylcyclohexanone or dihydrofuranone. In these two cases, products are formed which clearly arise from the ketene. This ketene formation explains the observed low quantum yields for triplet product formation in cyclohexanone. However, ketene formation can also be used to explain other quantum yield values observed for other ketones studied. When substitution occurs at the alpha position, the rate to form aldehyde becomes more competitive with ketene formation. Substitution at the beta position also probably affects competition between ketene and aldehyde formation. As substitution at the beta position becomes larger, the excited state yields mainly ketene. More work is needed in this area to determine quantitatively the magnitudes of these effects.

Pitts recently (65) made a quantitative examination on cyclopentanone and cyclohexanone. The values he obtained for lifetimes can be compared to those obtained in this study. The cyclopentanone values were directly comparable, but the value for cyclohexanone was not. Little experimental techniques were explained, so an absolute discrepancy is hard to determine. It is very likely, however, that the length of irradiation of the ketone solution explains the difference in data. The dependance of photolysis time on cyclohexanone has already been discussed.

Much investigation is still required for these types of systems to be completely understood. Substitution on the cyclopentanone ring would lead to very interesting results, with the expectation that the variations in reactivity and quantum yields could probably be explained in an analogous manner as the cyclohexanone system has been. One very interesting point arises from the fact that 2-phenylcyclohexanone cleavage may be affected by substitutions on the phenyl ring. The various enhancements and deactivations would prove to be a very worthwhile study. The larger ring systems such as in the case of cyclooctanone and cycloheptanone also show promise for future study. During this investigation, the larger ring systems were briefly examined. Photolysis of cycloheptanone for 114 hours yielded only an 8% disappearance of ketone, and photolysis of cyclooctanone for 144 hours gave only a 2% disappearance of ketone. These systems should be studied more completely, but it seems that as the ring size increases from a six-membered through an eight-membered ring, tendency for the cleavage of the alpha bond diminishes and trans-annular reactions take precedence.

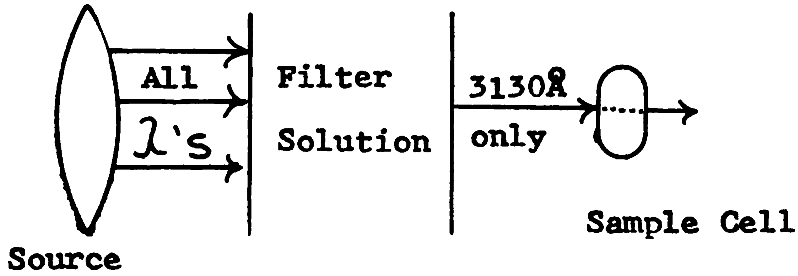
Experimental

I. Apparatus

All of the infra-red spectra were obtained on a Perkin-Elmer Model 237B recording spectrophotometer using sodium chloride cells. Nuclear magnetic resonance spectra were determined either in carbon tetrachloride or neat using a JEOLCO C-60H high resolution recording instrument with tetramethylsilane as an internal standard. The ultraviolet data were collected on a Spectronic "20" recording apparatus.

Vapor phase chromatography analyses were made using four different instruments: the F&M Model 700 with a thermal conductivity detector using a ¼" x 5' QF1 column, a Varian Series 1200 and an Aerograph Hy-Fi 600-D both equipped with flame ionization detectors using QF1 and Carbowax columns. A F&M Model 810 equipped with an Infotronics CRS-11HB electronic integrator was the fourth system used for analyses.

Two different experimental set-ups were used to carry out photolysis experiments. Photolytic experiments on a preparative scale were conducted in a water-cooled quartz immersion well using a 450 watt Hanovia medium pressure mercury arc lamp. All quantitative irradiation experiments were performed on a merry-go-round apparatus(69) equipped with a 450 watt Hanovia medium pressure mercury arc lamp contained in an aqueous solution of .002M potassium chromate with one percent potassium carbonate to filter out all but the 3130 Å mercury line. The entire unit was placed in a water bath contained at 25°C. A schematic representation of the unit is shown below:



II. Chemicals

Piperylene and isoprene were obtained from Aldrich and then purified by distillation. The 2,5-dimethyl-2,4-hexadiene, also obtained from Aldrich, was purified by repeated recrystallization from itself. All three quenchers were examined by vapor phase chromatography to insure maximum purity.

The solvent benzene and the internal standards were repeatedly treated with concentrated sulfuric acid, then with 10% aqueous sodium hydroxide solution, followed by several washings with distilled water and finally distilled over phosphorous pentoxide.

All of the ketones, except cyclopentanone, were obtained from Aldrich Chemical Co. Cyclopentanone was purchased from K & K Chemical Co. The ketones were purified by distillation through a 12" Vigereux column, except 2-phenylcyclohexanone which was purified by recrystallization from hexane. The ketones were checked for purity using vpc techniques.

III. Procedures

The product of photolysis of cyclopentanone, 4-pentenal was prepared in a similar manner to that of Srinivasan (10), except in the liquid phase rather than the gaseous phase. The material was collected on the F & M Model 776 Prepmaster Jr. using a 20% Carbowax column at 85°C. The infra-red spectra taken (See Figs. 12a & 12b) agrees with that described by Srinivasan. As a furthur diagnostic tool, an NMR was taken (See Figure 11) and also supported the structure of 4-pentenal.

The 5-hexenal, which is the product formed in the photolysis of cyclohexanone, was prepared in a similar manner described by Srinivasan (10). The aldehyde was again collected on the F & M Model 776 Prepmaster Jr. using a 20% Carbowax column at 100°C. The infra-red spectrum was taken and compared to that taken for 4-pentenal; they were superimposable. The NMR spectrum was also taken and was found to support the structure of 5-hexenal.

Twenty-five grams (.198 moles) of 2,6-dimethylcyclohexanone were diluted to 100 ml with benzene and placed in an immersion well. The solution was irradiated for 48 hours using a pyrex filter. The excess benzene was taken off by distillation, and the product collected on the F&M Model 776 already described, at 110°C. The infra-red spectrum (Figs. 13a & 13b) and NMR were taken. Analysis of these spectra supported the structure of 2-methyl-5-heptenal.

Twenty-five grams of 3-methylcyclohexanone were diluted to 100 ml with benzene and then photolyzed in an immersion well apparatus for 90 hours. The excess benzene was distilled off to concentrate the ketone and its products. The aldehydic product was seperated on the F&M Model 776 Prepmaster at 100°C using a 20% Carbowax column. An NMR spectra was taken to aid in identification of the product collected. As concluded by other workers (25,67), there was no indication of the other isomer, 5-methyl-5-hexenal.

Ten grams of 2-phenylcyclohexanone was dissolved in benzene and photolyzed for 6 hours. The benzene was taken off using a rotary aspirator. Attempts to isolate and identify this product of photolysis using the F&M Model 776 Prepmaster were unsucessful.

The method of H.O. House and V. Kramer (68) was used to prepare 2,2-dimethylcyclohexanone. The product was isolated using a F&M Model 776 preparative chromatograph at 85°C with a 20% Carbowax column.

B. Quenching Studies

For the 2,2-dimethylcyclohexanone, one stock solution 0.67M in ketone and 0.035M in pentadecane, as standard, was prepared by weighing the appropriate amount of ketone and standard in a 25ml volumetric flask and diluting to volume with benzene. Stock solution 0.10M in piperylene was prepared similarly. A 2ml portion of the ketone stock solution was pipetted into each of seven 10ml volumetric flasks, one of which was immediately filled to volume with solvent. Quantities of 1 to 3, 5 and 8 ml of each of the quancher solutions were pipetted into each of the other flasks before they were diluted to volume. Then 3.0ml of each diluted solution was placed in seperate pyrex tubes with a syringe. The tubes were standard 13x100mm culture tubes which had been washed and dried before being constricted about one inch from the top to allow sealing. The tubes with the samples in them were attached to a vacuum line and put through three freeze-pump-thaw cycles before being sealed in vacuo at .005mm.

Samples were prepared quite similarly for the other ketones except using different standards, for usable vpc analysis, and different concentrations of quencher for measurable Stern-Volmer plots.

In any given run, degassed tubes containing various concentrations of quencher were irradiated in parallel with two samples containing only ketone and standard in benzene solution, all for the same amount of time. Irradiations were performed in the merry-go-round apparatus, already mentioned, consisting of a rotating turntable with the light source and filters at the center and windows of identical area allowing radiation to enter the various samples ports. The entire apparatus was immersed in a water bath, and the temperature during irradiation was held at 25°C.

The percentages of singlet reaction were determined for cyclopentanone, cyclohexanone, and 2-methylcyclohexanone. Stock solutions of these ketones and their respective standards were prepared similarly to the method already described. Tubes containing no quencher and others containing high concentrations of quencher were prepared and irradiated in an identical manner. From analysis of these solutions, the per cent singlet reaction can be calculated.

The experimental results are shown here in Tables XVI- XXXIV.

Table XVI

Quenching of 0.2M Cyclopentanone at High Conversion

Standard=0.05M tridecane
Irradiation Time= 68 hours
Per Cent conversion= 54%
VPC Conditions: Injector=200°C
Detector=250°C
Oven=110°C
Column= FFAP
He flow rate= 50 ml/min
Apparatus: F&M Model 700

	K/S[a]	%Reacted	%Triplet Reacted	ϕ_0/ϕ_a[b]
0M(unphotolyzed)	1.868	0		
0 M	.860	54.0	46.7	1.000
5×10^{-3}M	.951	49.1	42.5	1.115
1×10^{-2}M	1.003	46.4	40.3	1.192
2×10^{-2}M	1.116	40.3	34.7	1.407
3×10^{-2}M	1.171	37.3	32.2	1.541
4×10^{-2}M	1.250	33.1	28.6	1.788
5×10^{-2}M	1.279	31.5	27.3	1.900

[a] Chromatographic area molar ratio of Ketone/Standard.

[b] These values represented here have had the singlet reaction subtracted out.

See Figure 1 for Stern-Volmer plot of results.

Table XVII

Singlet Reaction of Cyclopentanone

Concentration of ketone=0.2M
Standard=0.05M dodecane
VPC Conditions: Same as Table XVI

[Isoprene]	Irradiation Time	% Ketone Reacted	K/S[a]
0M	0 hours	0	1.872
0M	54 hours	53.	.876
0M	42 hours	42.	1.071
2M	96 hours	12.	1.650[b]
2M			

[a] This is the chromatographic area ratio of ketone to standard peaks.

[b] Average of two runs

Table XVIII

Photolysis of 0.15M Cyclopentanone at Low Conversion (Run 1)

Standard=0.004M tridecane
Irradiation Time= 5½ hours
Conversion= 8%
VPC Conditions: Injector=180°C
Detector=195°C
Oven= 35°C-75°C at 2°C/min
Column= 4%QF1;1% Carbowax
He flow rate= 25 ml/min
Apparatus: Varian "1200" Aerograph

[Piperylene]	P/S Area Ratio	+[P][a]	ϕ_0/ϕ_a
0M	.897	.0142	1.00
5.01×10^{-3}M	.665	.0104	1.35
1.02×10^{-2}M	.586	.0093	1.53
2.04×10^{-2}M	.491	.0079	1.84
3.06×10^{-2}M	.358	.0057	2.51

[a] Assuming area to molar ratio of ketone is the same for its aldehydic product. Later experiments showed this to be true.

Table XIX

Photolysis of 0.2M Cyclopentanone at Low Conversion (Run 2)

Standard= .005M Tridecane
Irradiation Time= 6 hrs.
Conversion= 9%
VPC Conditions: Injector= 190°C
Detector= 200°C
Oven= 30°-75°C at 2°C/min
He flow rate= 25 ml/min
Apparatus: Varian Series "1200" using
a 4% QF1 & 1% Carbowax
column

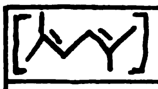
[Piperylene]	P/S Area Ratio	+[P][a]	$\emptyset_o/\emptyset_a$
0 M	.533	.0169	1.00
5.1×10^{-3} M	.415	.0132	1.28
1.1×10^{-2} M	.351	.0111	1.52
2.2×10^{-2} M	.271	.0086	1.96
3.3×10^{-2} M	.216	.0067	2.46

[a] Assuming the area to molar ratio of ketone is the same for its aldehydic product. Later experiments showed this to be true.

Table XX

Photolysis of 0.2 M Cyclohexanone at High Conversion

Standard= .05M Tetradecane
Irradiation Time= 90 hrs.
Conversion= 43%
VPC Conditions: Injector= 185°C
Detector= 250°C
Oven= 40°C-85°C at 2°C/min
Column= FFAP
He flow rate= 50 ml/min
Apparatus: F&M Model "700"

	K/S[a]	%K Reacted	% Triplet Formed	ϕ_o/ϕ_a[b]
0M(Unphotolyzed)	2.016	0%	0%	
0M	1.142	43.4 %	38.7 %	1.000
1.08×10^{-3}M	1.333	33.9 %	29.8 %	1.324
2.16×10^{-3}M	1.419	29.7 %	26.1 %	1.552
3.24×10^{-3}M	1.440	28.6 %	25.2 %	1.620
4.32×10^{-3}M	1.469	27.2 %	23.8 %	1.725

[a] Chromatographic area ratio of ketone to standard

[b] These values have had the singlet reaction subtracted out.

See Figure 3 for Stern-Volmer plot of results for cyclohexanone photolysis.

Table XXI

Singlet Reaction of Cyclohexanone

Concentration of Ketone= 0.2M
Standard= .05M Tridecane
VPC Conditions: Same as in Table XX except
oven is at 110°C

[Piperylene]	Irradiation Time	% Ketone Reacted	K/S[a]
0 M	0 hrs.	0	1.958
0 M	24 hrs.	18.2 %	1.602
0 M	54 hrs.	27.2 %	1.425
.2 M	97 hrs.	7.1 %[b]	1.820
.2 M	97 hrs.		

[a] These values represent area ratios for ketone to standard

[b] Average of two runs

Table XXII

Photolysis of 0.1 M Cyclohexanone at Low Conversion (Run 1)

Standard= .005 M Tridecane
Irradiation Time= 9 hrs.
Conversion= 11 %
VPC Conditions: Injector= 185°C
Detector= 200°C
Oven= 70°C
Column= 4% QF1 & 1% Carbowax
He flow rate= 25 ml/min
Apparatus: Varian "1200"

[Piperylene]	P/S Area Ratio	+[P] [a]	ϕ_o/ϕ_a
0 M	.489	.0106	1.00
1×10^{-3}M	.422	.0092	1.16
2×10^{-3}M	.376	.0081	1.30
3×10^{-3}M	.331	.0072	1.478

[a] Assuming area to molar ratio for ketone is the same for its aldehydic product.

Table XXIII

Photolysis of 0.2M Cyclohexanone at Low Conversion(Run 2)

Standard= .005M Tridecane
Irradiation Time= 6 hrs.
Conversion= 7 %
VPC Conditions: Injector= 190°C
Detector= 200°C
Oven= 40°C-85°C at 2°C/min
Column= 4% QF1 & 1% Carbowax
He flow rate= 25 ml/min
Apparatus: Varian "1200"

[Piperylene]	P/S Area Ratio	+[P] [a]	ϕ_o/ϕ_a
0 M	.371	.0097	1.000
1.1×10^{-3}M	.318	.0083	1.166
2.2×10^{-3}M	.278	.0072	1.336
4.4×10^{-3}M	.224	.0059	1.657

[a] Assuming the area to molar ratio for the ketone is the same for its aldehydic product.

Table XXIV

Photolysis of 0.2 M 2-Methylcyclohexanone at High Conversion

Standard= .05M Tetradecane
Irradiation Time= 75 hrs.
Conversion= 77 %
VPC Conditions: Injector= 190°C
Detector= 250°C
Oven= 105°C
Column= FFAP
He flow rate= 50 ml/min
Apparatus: F & M Model "700"

[Isoprene]	K/S[a]	%K Reacted	% Triplet Formed	ϕ_o/ϕ_a[b]
OM(Unphotolyzed)	2.089	0 %	0 %	————
0 M	.472	77 %	67.7 %	1.000
5.02×10^{-3}M	.504	75.8 %	66.7 %	1.021
1.03×10^{-2}M	.561	73 %	64.3 %	1.069
2.06×10^{-2}M	.630	69.8 %	61.5 %	1.128
3.09×10^{-2}M	.722	65.5 %	57.6 %	1.217
2 M	1.859	11.1 %	0 %	————

[a] Chromatographic area ratio of ketone to standard

[b] The singlet reaction has been subtracted out of these values

Table XXV

Photolysis of 0.1 M 2-Methylcyclohexanone at Low Conversion(Run 1)

Standard= .005M Tetradecane
Irradiation Time= 6 hrs.
Conversion= 9 %
VPC Conditions: Injector= 180°C
Detector= 200°C
Oven= 80°C
Column= 4% QF1, & 1% Carbowax
He flow rate= 25 ml/min
Apparatus: Varian "1200"

[Piperylene]	P/S Area Ratio	+[P] [a]	ϕ_o/ϕ_a
0 M	1.273	.0117	1.000
1.1×10^{-2}M	1.127	.0104	1.130
2.2×10^{-2}M	1.015	.0093	1.250
3.3×10^{-2}M	.940	.0086	1.350
1.5 M	0.0	-----	-----

[a] Assuming area to molar ratio for ketone is the same for its aldehydic product

Table XXVI

Photolysis of 0.2M 2-Methylcyclohexanone at Low Conversion(Run 2)

Standard= .005M Tetradecane
Irradiation Time= 9 hrs.
Conversion= 12 %
VPC Conditions: Same as in Table XXV, except
Oven is 85°C

[Piperylene]	P/S Area Ratio	+[P] [a]	ϕ_o/ϕ_a
0 M	1.451	.0187	1.000
1.1×10^{-2}M	1.331	.0171	1.090
2.2×10^{-2}M	1.138	.0147	1.280
4.4×10^{-2}M	1.051	.0135	1.446

[a] Assuming area to molar ratio for the ketone is the same for its aldehydic product

See Figure 4 for Stern-Volmer plot of these results.

Table XXVII

Photolysis of 0.2 M 3-Methhlcyclohexanone at High Conversion

Standard= .05M Tetradecane
Irradiation Time= 93 hrs.
Conversion= 25 %
VPC Conversion: Injector= 195°C
Detector= 250°C
Oven= 115°C
Column= FFAP
He flow rate= 50 ml/min
Apparatus: F & M Model "700"

	K/S[a]	% K Reacted	% Triplet Formed	ϕ_o/ϕ_a[b]
OM(Unphotolyzed)	2.125	0%	0 %	-----
0 M	1.586	25.4 %	23.3 %	1.000
1.1×10^{-3}M	1.691	20.4 %	18.7 %	1.270
2.2×10^{-3}M	1.755	17.4 %	15.9 %	1.522
3.3×10^{-3}M	1.766	16.8 %	15.4 %	1.792
4.4×10^{-3}M	1.902	15.2 %	13.9 %	2.030

[a] Chromatographic area ratios of ketone to standard

[b] The singlet reaction has been subtracted out of these values

Table XXVIII

Photolysis of 0.15M 3-Methylcyclohexanone at High Conversion

Standard= .05 Tetradecane
Irradiation Time= 114 hrs.
Conversion= 42%
VPC Conditions: Injector= 200°C
Detector= 250°C
Oven= 110°C
Column= FFAP
He flow rate= 50 ml/min
Apparatus: F & M Model "700"

[Piperylene]	K/S[a]	% K Reacted	% Triplet Formed	ϕ_o/ϕ_a[b]
OM(unphotolyzed)	2.051	0 %	0 %	-------
0 M	1.185	42 %	38.6%	1.000
1.04×10^{-3}M	1.273	37.9 %	34.8%	1.125
2.08×10^{-3}M	1.358	33.8 %	31.0%	1.278
3.12×10^{-3}M	1.429	30.3 %	27.8%	1.443

[a] Chromatographic area ratio of ketone to standard.

[b] The singlet reaction, equal to 8.3%, has been subtracted.

Table XXIX

Photolysis of 0.1 M 3-Methylcyclohexanone at Low Conversion

Standard= .005M Tetradecane
Irradiation Time= 12 hrs.
Conversion= 11 %
VPC Conditions: Injector= 185°C
Detector= 200°C
Oven= 110°C
Column= 4% QF1 & 1% Carbowax
He flow rate= 25 ml/min
Apparatus: Varian "1200"

[Piperylene]	P/S Area Ratio	+[P]	ϕ_o/ϕ_a
0 M	.149	.0109	1.00
2.12×10^{-3}M	.106	.0077	1.41
3.18×10^{-3}M	.091	.0066	1.64
4.24×10^{-3}M	.076	.0056	1.96
.5 M	.001	.0009	----

See Figure 5 for Stern-Volmer plot of these results on 3-methylcyclohexanone.

Table XXX

Photolysis of 0.1 M 3,5-Dimethylcyclohexanone at Low Conversion

Standard= .005 M Pentadecane
Irradiation Time= 22 hrs. (full arc)
Conversion= 10 %
VPC Conditions: Injector= 195°C
Detector= 200°C
Oven= 30-100°C at 2°C/min
Column= 4% QF1 & 1% Carbowax
He flow rate= 25 ml/min
Apparatus: Varian "1200"

[Piperylene]	P/S Area Ratio	+[P][a]	ϕ_o/ϕ_a
0 M	.0806	.0083	1.000
1.01×10^{-3}M	.0666	.0068	1.210
2.02×10^{-3}M	.0566	.0058	1.421
3.03×10^{-3}M	.0500	.0052	1.610
.5 M	.003	.0003	26.8

[a] Assuming area to molar ratio for ketone to be the same for its aldehydic product.

See Figure 6 for Stern-Volmer plot of these results.

Table XXXI

Photolysis of 0.1 M 3,3,5-Trimethylcyclohexanone at Low Conversion

Standard= .005M Pentadecane
Irradiation Time= 40 hrs.(full arc)

Conversion= 5 %
VPC Conditions: Injector= 185°C
Detector= 200°C
Oven= 60-100°C at 2°C/min
Column= 4% QF1 & 1% Carbowax
He flow rate= 25 ml/min
Apparatus: Varian "1200"

[Piperylene]	P/S Area Ratio	+[P][a]	ϕ_o/ϕ_a
0 M	.0680	.0027	1.000
1×10^{-3} M	.0569	.0023	1.194
2×10^{-3} M	.0484	.0019	1.404
3×10^{-3} M	.0424	.0017	1.605
.4 M	.0000	------	------

[a] Assuming area to molar ratio for ketone to be the same for its aldehydic product.

See Figure 7 for Stern-Volmer plot of results in Table XXXI.

Table XXXII

Photolysis of 0.1 M 2,6-Dimethylcyclohexanone at Low Conversion

Standard= .005M Tridecane
Irradiation Time= 4 hrs.
Conversion= 13 %
VPC Conditions: Injector= 190°C
Detector= 200°C
Oven= 65°C
Column= 4% QF1 & 1% Carbowax
He flow rate= 25 ml/min
Apparatus: Varian "1200"

[Piperylene]	P/S Area Ratio	+[P] [a]	ϕ_o/ϕ_a
0 M	1.712	.0141	1.000
1×10^{-2} M	1.628	.0134	1.052
2×10^{-2} M	1.545	.0127	1.109
3×10^{-2} M	1.471	.0121	1.164
4 M	-----	-----	-----

[a] Assuming area to molar ratio for ketone to be the same for its aldehydic product

See Figure 8 for Stern-Volmer plot of results in Table

Table XXXIII

Photolysis of 0.1 M 2-Phenylcyclohexanone at Low Conversion

Standard= .005M Heptadecane
Irradiation Time= 3 hrs.
Conversion= 7 %
VPC Conditions: Same as in previous Table except Injector= 200°C and oven= 155°C

[Piperylene]	P/S Area Ratio	P/S - S_s [a]	+[P] [b]	ϕ_o/ϕ_a
0 M	.0775	.0755	.00101	1.000
1.1×10^{-2}M	.0665	.0645	.00085	1.170
2.2×10^{-2}M	.0598	.0578	.00078	1.321
3.3×10^{-2}M	.0510	.0490	.00066	1.521
2 M	.002	-----	------	-----

[a] Chromatographic area ratio minus the singlet reaction.

[b] Assuming area to molar ratio for ketone to be the same for its aldehydic product.

See Figure 9 for Stern-Volmer plot of results in Table XXXIII.

Table XXXIV

Photolysis of 0.1 M 2,2-Dimethylcyclohexanone at Low Conversion

Standard= .005M Pentadecane
Irradiation Time= 2 hrs.
Conversion= 8.1 %
VPC Conditions: Injector= 190°C
Detector= 200°C
Oven= 65-100°C at 2°C/min
Column= 4% QF1 & 1% Carbowax
He flow rate= 100 ml/min
Apparatus: F & M Model "810"

[Piperylene]	P/S Area Ratio	$P/S-S_s$[a]	+[P][b]	ϕ_o/ϕ_a
0 M	1.646	1.631	.0137	1.000
1×10^{-2} M	1.604	1.589	.0133	1.027
2×10^{-2} M	1.557	1.542	.0129	1.057
3×10^{-2} M	1.517	1.502	.0126	1.084
5×10^{-2} M	1.446	1.431	.0120	1.141
8×10^{-2} M	1.346	1.331	.0112	1.224

[a] Chromatographic area ratio minus the singlet reaction

[b] Assuming area to molar ratio for the product is the same as the parent ketone

See Figure 10 for Stern-Volmer plot of these results.

A 0.2 M solution of cycloheptanone containing .05M tridecane was photolyzed for 117 hours in the presence of various concentrations of quencher. After that time, the tubes were analyzed as follows.

K/S for Unphotolyzed solution= 2.047
K/S for Photolyzed solution= 1.850

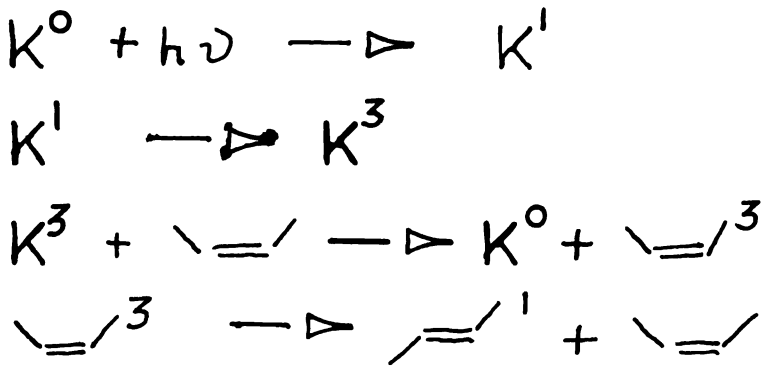
A detailed set of data was not collected for this ketone.

A 0.2 M solution of cyclooctanone containing .05 M hexadecane in benzene was prepared and photolyzed in a similar manner to all ketones studied. The system was photolyzed for 144 hours with only 2.3% reaction occuring. A detailed set of data was not collected for this ketone.

C. Quantum Yields

Ten milliliter volumetrics were weighed and then charged with different ketones and their respective standards, weighed to the nearest ten-thousandth gram. The volumetrics were then diluted to volume with purified benzene. A 3 ml portion of each was pipetted into seperate pyrex tubes with a syringe. The tubes were the standard 13x100 mm culture tubes which had been washed and dried before being constricted about one inch from top to allow sealing. The tubes were degassed by freeze-pump-thaw cycles before being sealed in vacuo at .005 mm.

In order to measure the quantum yields accurately, a precise actinometry method had to be used. Hammond and co-workers (66) made an extensive study on intersystem crossing efficiencies of various substrates. They developed an accurate method for measuring the quantum yields of triplets in solution. In their experiments, the triplets could be determined by following the isomerization of some olefin from its trans- to cis- form or vice versa, as shown below:



In our experiments, the sensitizor was acetone because it is known to give 100% triplets in solution (70). The amount of these triplets formed was followed by the photoisomerization of cis-piperylene to its trans isomer. The equation used for this calculation is shown below:

$$\beta = [A]\,\mathrm{LN}\left(\alpha/\alpha-\beta'\right)$$

where, β is the conversion of cis to trans without back reaction,

α is the conversion at the stationary state for the olefin (for cis to trans piperylene = .555)

β' is the conversion of cis to trans measured experimentally,

$[A]$ is the original concentration of the cis-piperylene.

The per cent conversion of cis- to trans-piperylene was followed on a 25% 1,2,3-triscyanoethoxyethane ($\beta\beta\beta$) at 50°C.

The actinometer tubes were prepared by weighing acetone and cis-piperylene to the nearest ten-thousandth gram. The volumetrics were diluted to volume with purified n-hexane. A 3ml portion was then placed into pyrex tubes and degassed, as in previous experiments. These tubes were photolyzed in a merry-go-round apparatus simultaneously with the ketones to be studied. With the actinometer tubes present, it is possible to determine the intensity of the 450 watt Hanovia mercury arc lamp.

The results are given in the following tables.

Table XXXV

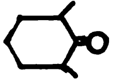
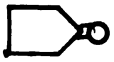
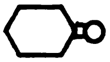
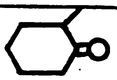
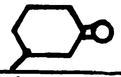
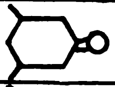
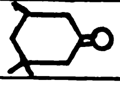
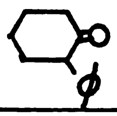
Actinometer Analysis for Quantum Yield of Ketone Disappearance at Low Conversion

[cis-Piperylene]	Time Irradiated	% Converted	$\ln \frac{.555}{.555-\%\text{Conv.}}$	I_o/hr
.133	1hr 35min	9.47 %	.1188	.0158[a]
.133	1hr 35min	9.52 %		

[a] Average of two runs

Table XXXVI

Relative Quantum Yields for Disappearance of Ketone at High Conversions

Ketone	Initial Concentration	% Reaction	% Light[a] Absorbed	Time[b]	-K/hr.	ϕ_{-k}[c]
	.1058M	61 %	89.5%	12½hrs	.0051	1.00
	.1118M	62 %	97.0%	25½hrs	.0027	.435
	.1112M	28 %	88.2%	25½hrs	.0012	.218
	.1070M	64 %	89.7%	15 hrs	.0046	.88
	.1000M	21 %	84.6%	25½hrs	.00083	.153
	.1068M	11 %	87.5%	25½hrs	.00049	.094
	.1020M	7.3%	87.1%	25½hrs	.00029	.052
	.1050M	51 %	97.1%	12½hrs	.0043	.685

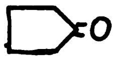
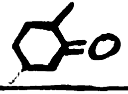
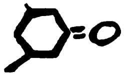
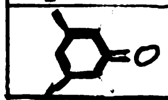
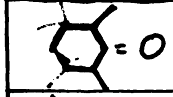
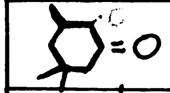
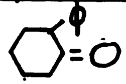
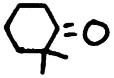
[a] Per cent of light absorbed by respective concentrations.

[b] Photolysis time of solutions

[c] Relative to 2,6-Dimethylcyclohexanone

Table XXXVII

Quantum Yields for Disappearance of Ketone at Low Conversion

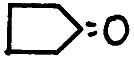
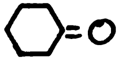
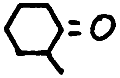
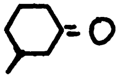
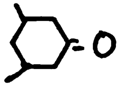
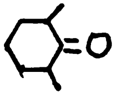
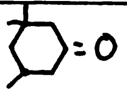
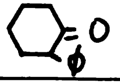
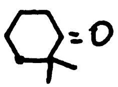
Ketone	Concentration	Standard	$(K/S)_i$	$(K/S)_f$	% -K	Time (hrs.)	-K/hr.	% Light Absorbed	Corr I_o [a]	ϕ_{-k}
	.106 M	.042 M tridecane	.691	.525	24	6	.00424	96.4	.0152	.28
	.106 M	.042 M tridecane	.858	.743	13.6	7.75	.00176	86.6	.0137	.13
	.118 M	.0421 M tetradecane	1.075	.878	18.3	3	.0072	92.1	.0145	.50
	.107 M	.0421 M tetradecane	1.146	.975	14.9	14	.00114	86.4	.0136	.08
	.102 M	.042 M pentadecane	1.089	.963	11.6	$26\frac{1}{4}$	.00045	85.2	.0134	.033
	.114 M	.042 M undecane	1.351	1.065	21	3	.0081	91.2	.0144	.56
	.104 M	.052 M hexadecane	.943	.865	8.3	$26\frac{1}{4}$	.00033	87.5	.0138	.024
	.106 M	.051 M heptadecane	1.091	.846	22.4	3	.0079	97.2	.0154	.51
	.103 M	.042 M undecane	.979	.762	22.0	3	.00621	89.8	.0116 [b]	.54

[a] The absolute I_o = .0158/hr. The values given here have been corrected since the per cent of the light absorbed is not 100 %.

[b] The absolute I_O = .0130/hr. for this ketone only.

Table XXXVIII

Quantum Yields for Product Formation

Ketone	Concentration	Standard	Time (hrs.)	-% K	[Prod]	[Prod]/hr	% Light^a Absorbed	ϕ_{+p}
	.1089 M	.045 M tridecane	3	9.5	.0092M	.00307M	96.7	.24
	.1068 M	.043M tridecane	2	5.4	.0021M	.00104M	86.8	.09
	.1027M	.043M tetradecane	1	6.4	.0050M	.00501M	89.1	.42
	.1051 M	.044M tetradecane	4	6.2	.0016M	.00039M	86.1	.034
	.1033 M	.043M pentadecane	12.5	5.7	.0008M	.00007M	86.8	.005
	.1022 M	.044M undecane	1	6.1	.0048M	.00481M	88.8	.40
	.0990 M	.051M hexadecane	12.5	2.7	.0003M	.00002M	86.6	.002
	.0861 M	.051M heptadecane	1	13.0	.0005M	.00053M	94.7	.042
	.1010M	.037M undecane	2	8.2	.0096M	.00478M	88.6	.42^b

^aI_o = .0133/hr.

^bI_o = .0130/hr. for this ketone only.

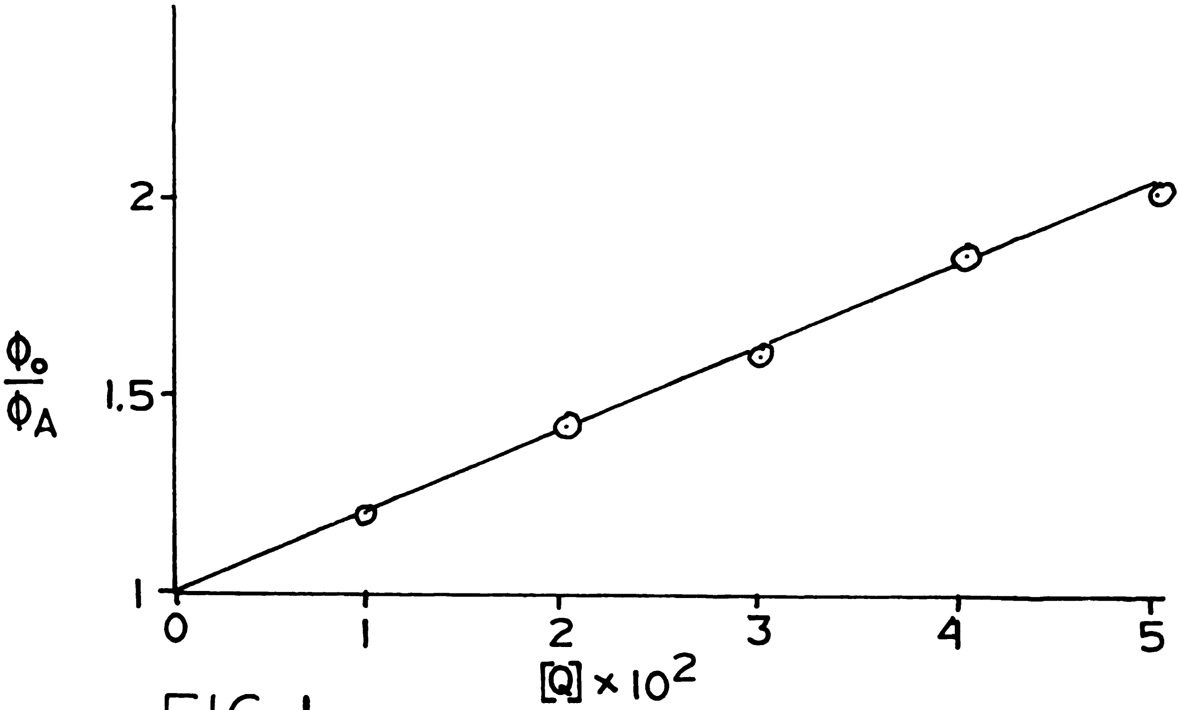


FIG. 1 STERN-VOLMER PLOT FOR QUENCHING OF CYCLOPENTANONE AT HIGH CONVERSION

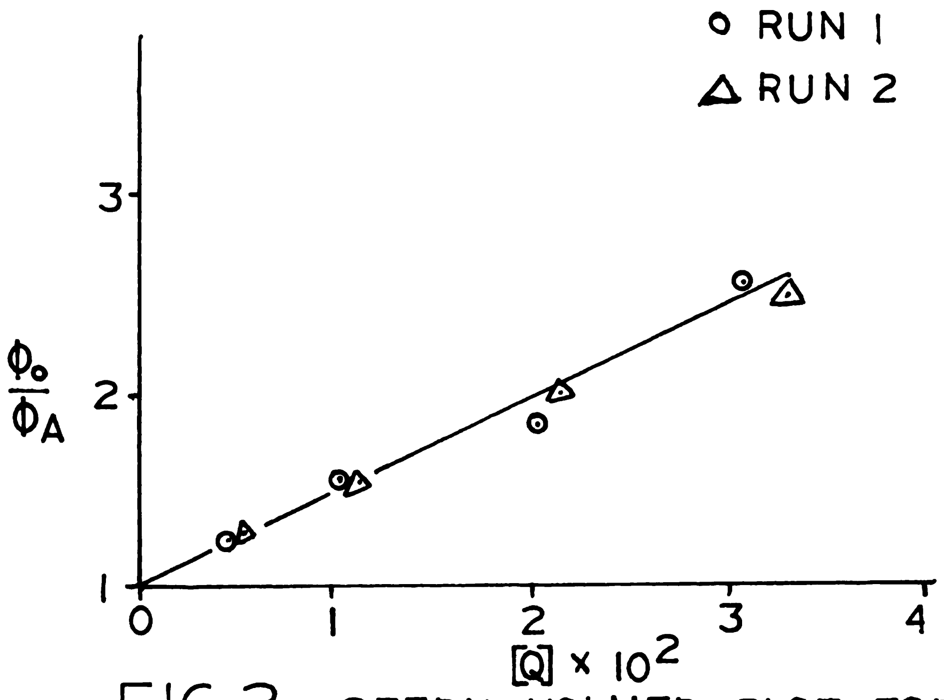


FIG. 2 STERN-VOLMER PLOT FOR QUENCHING OF CYCLOPENTANONE AT LOW CONVERSION

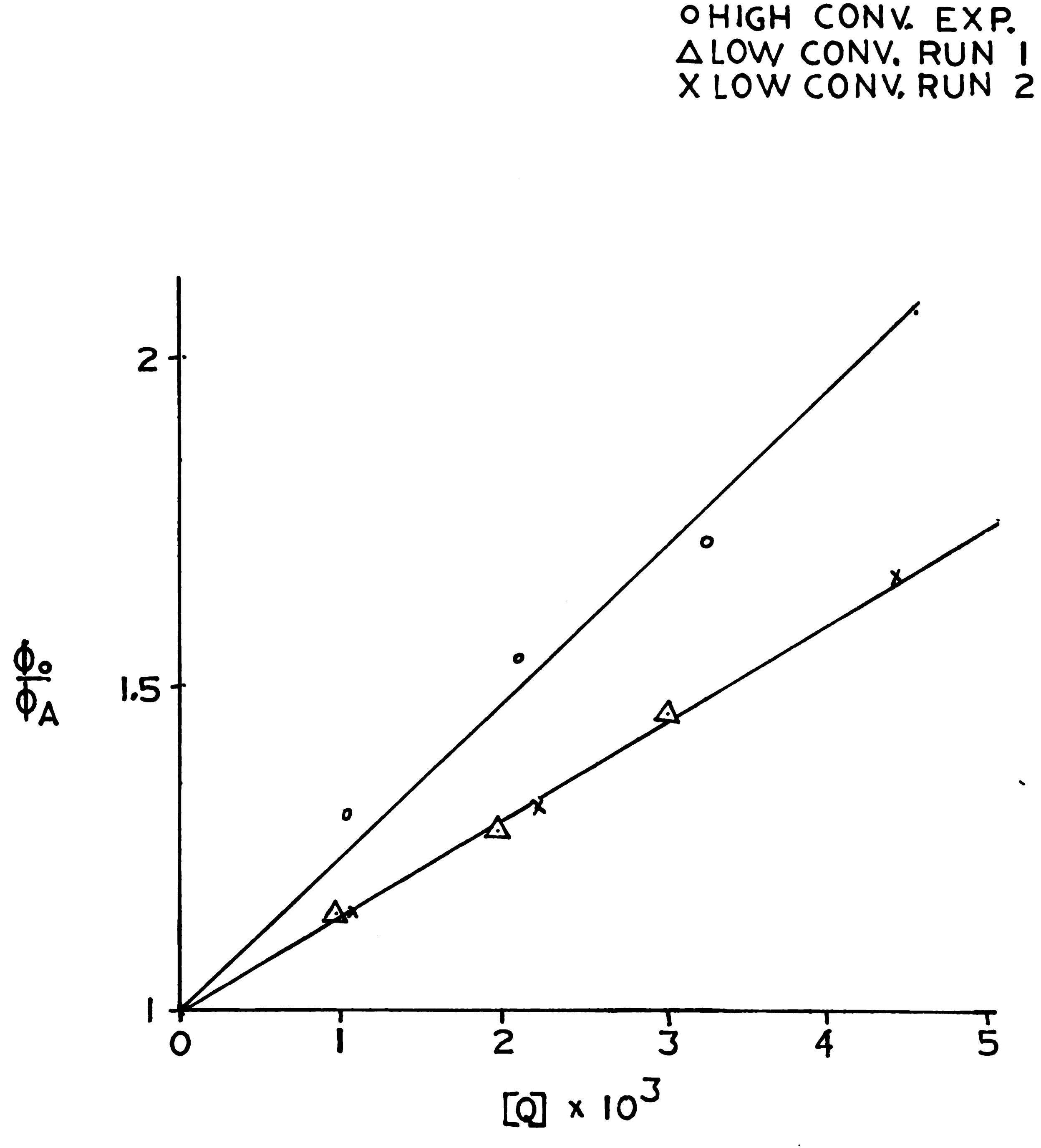


FIG.3 STERN—VOLMER PLOTS FOR QUENCHING OF CYCLOHEXANONE AT HIGH AND LOW CONVERSIONS

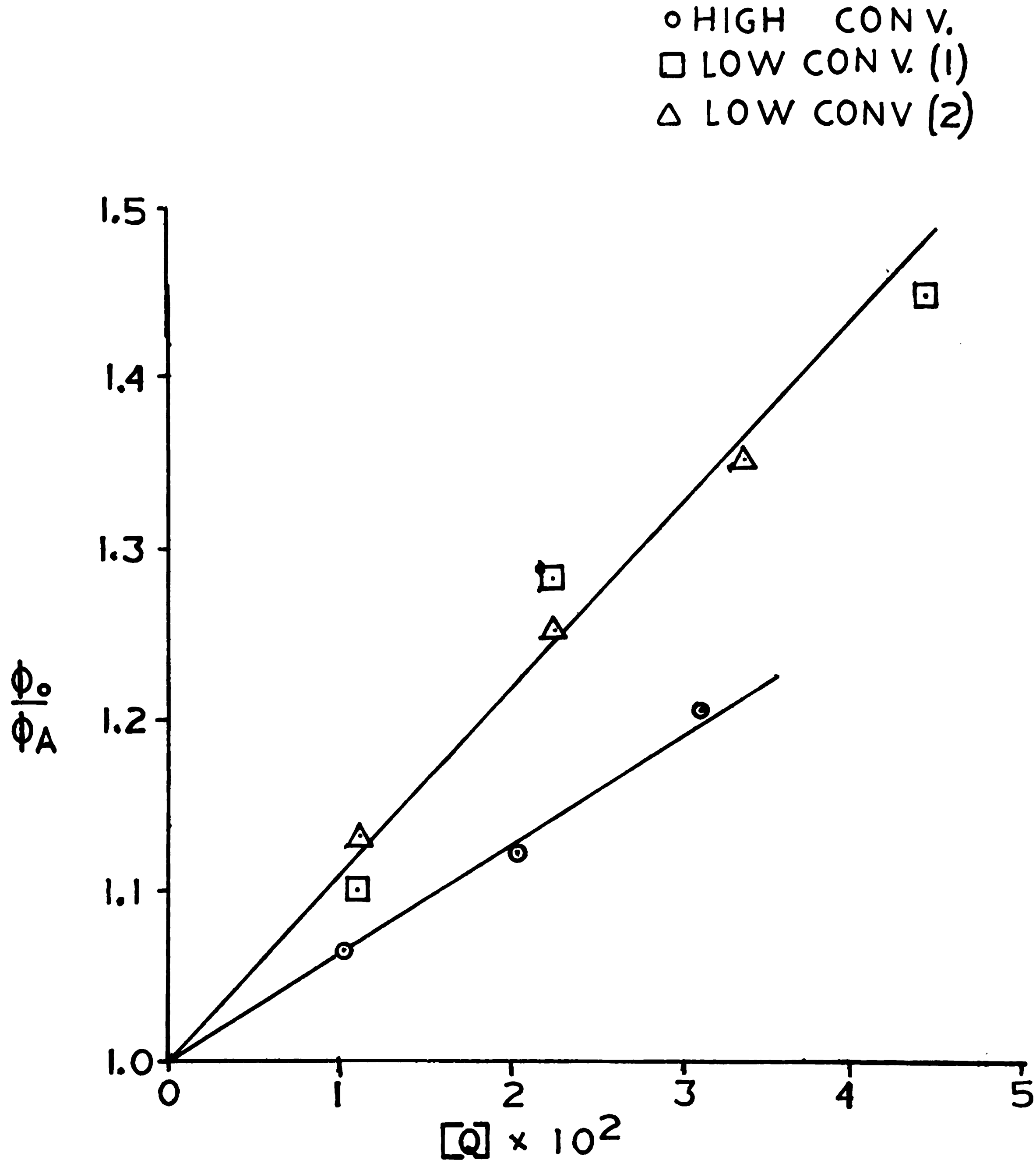


FIG. 4 STERN–VOLMER PLOTS FOR QUENCHING OF 2-METHYLCYCLOHEXANONE AT HIGH AND LOW CONVERSIONS

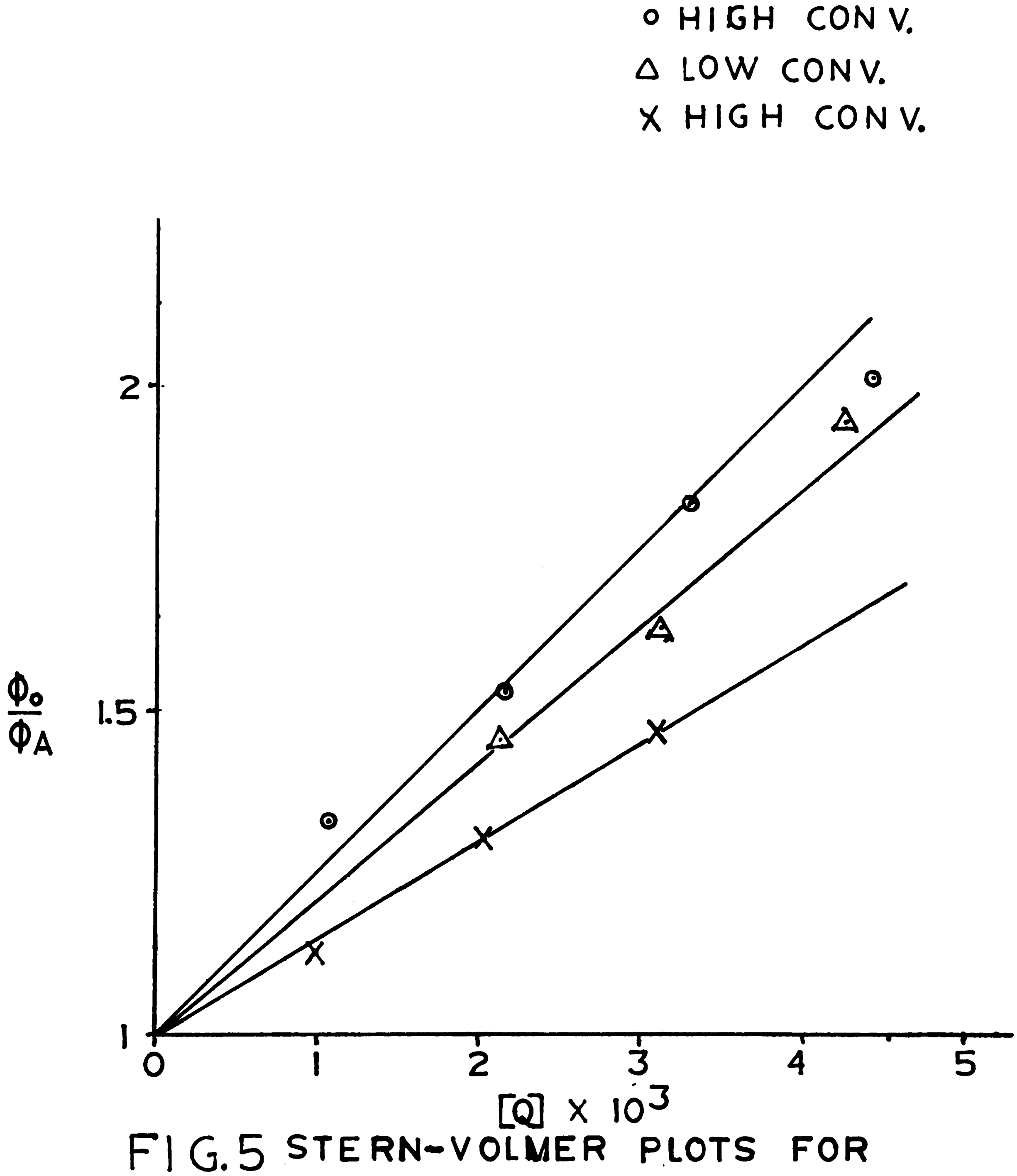


FIG. 5 STERN-VOLMER PLOTS FOR QUENCHING OF 3-METHYLCYCLOHEXANONE AT HIGH AND LOW CONVERSIONS

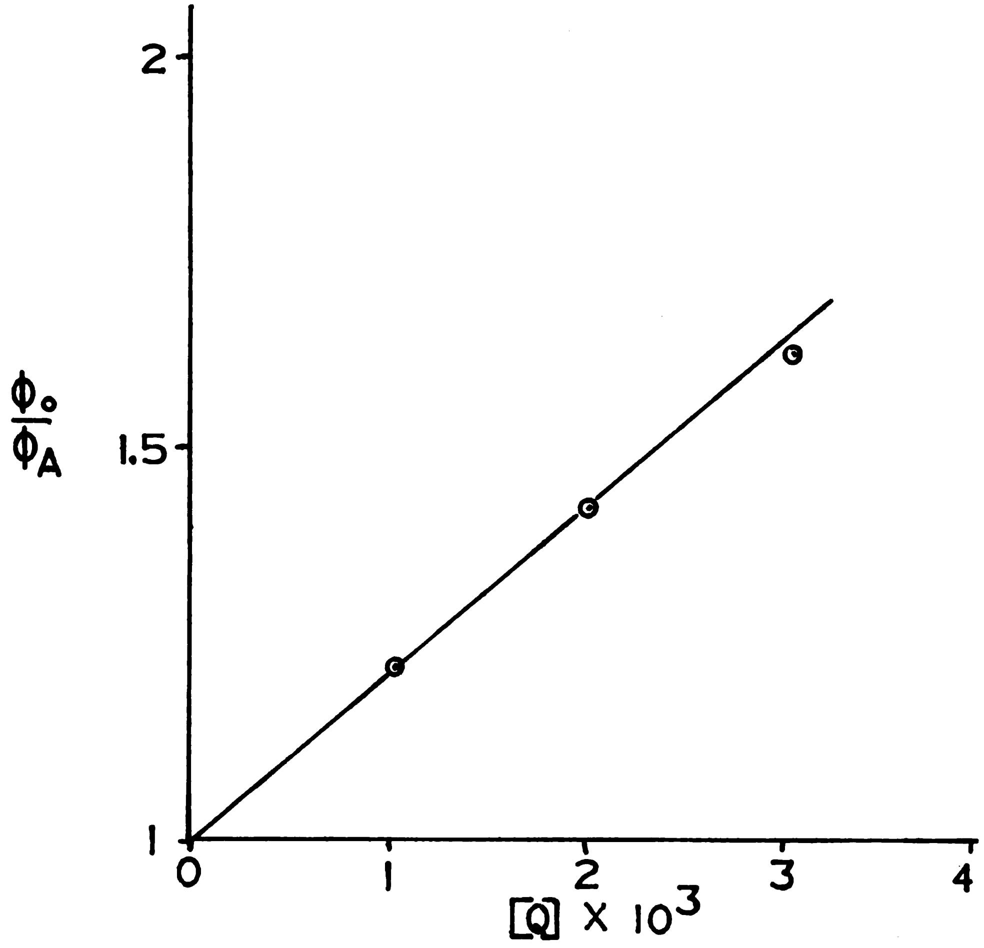


FIG.6 STERN-VOLMER PLOT FOR QUENCHING OF 3,5-DIMETHYLCYCLOHEXANONE

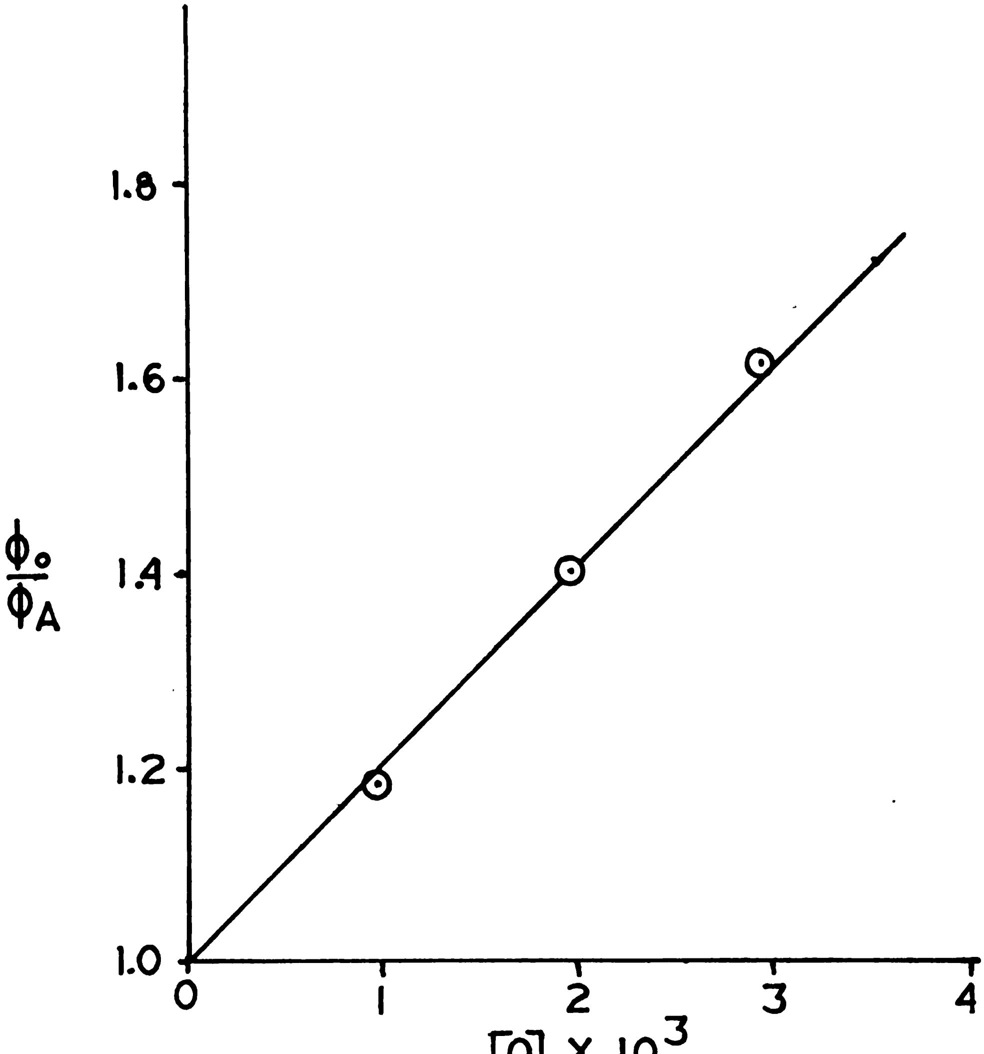


FIG.7 STERN-VOLMER PLOT FOR QUENCHING OF 3,3,5-TRIMETHYLCYCLOHEXANONE

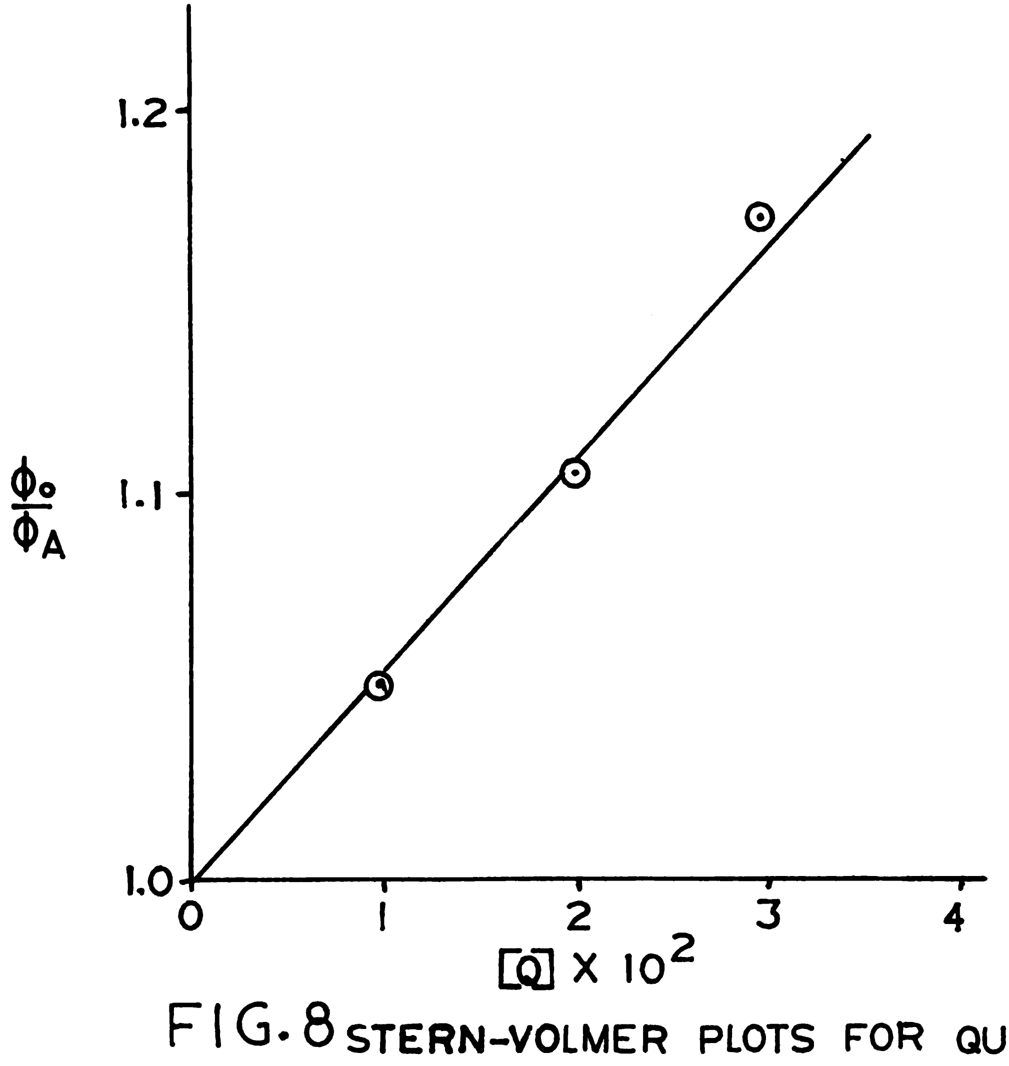


FIG. 8 STERN-VOLMER PLOTS FOR QUENCHING OF 2,6-DIMETHYLCYCLOHEXANONE

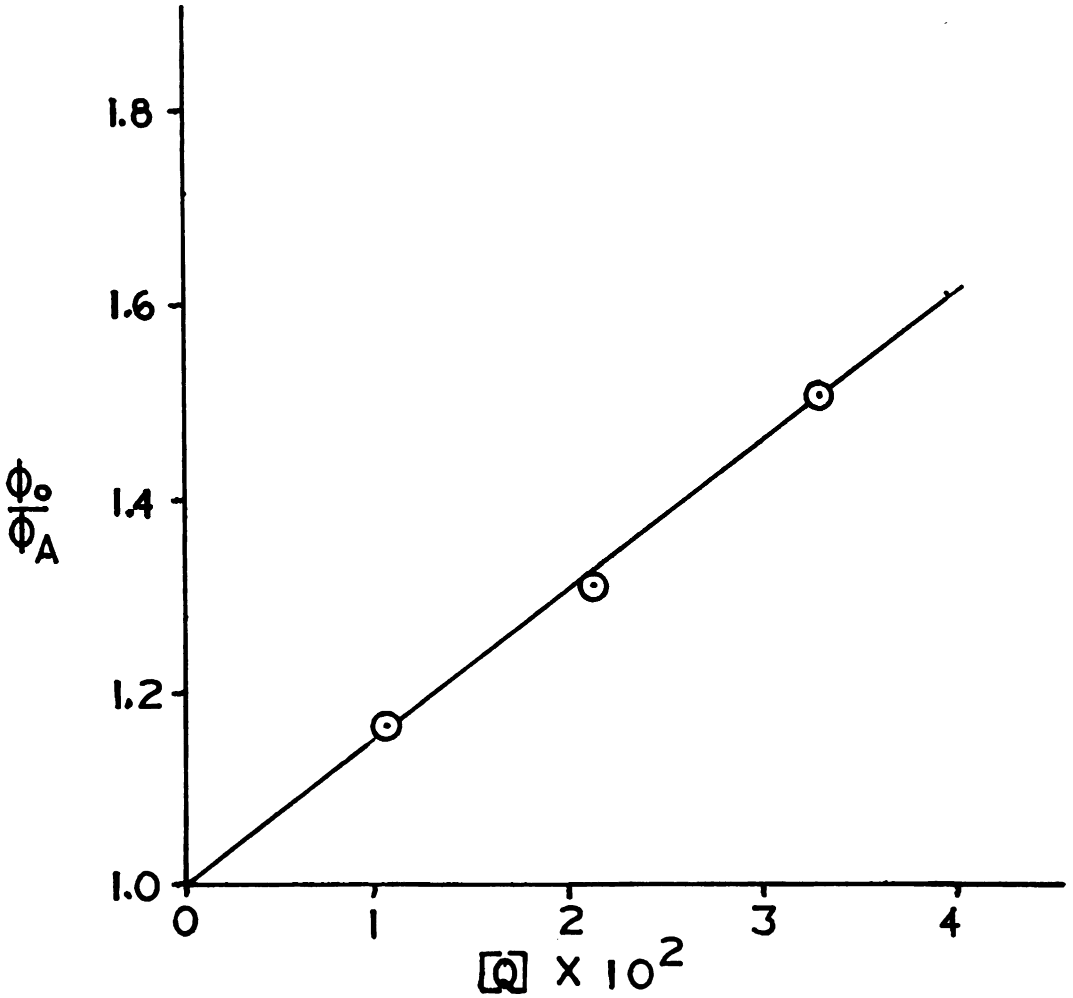


FIG. 9 STERN-VOLMER PLOT FOR QUENCHING OF 2-PHENYLCYCLOHEXANONE

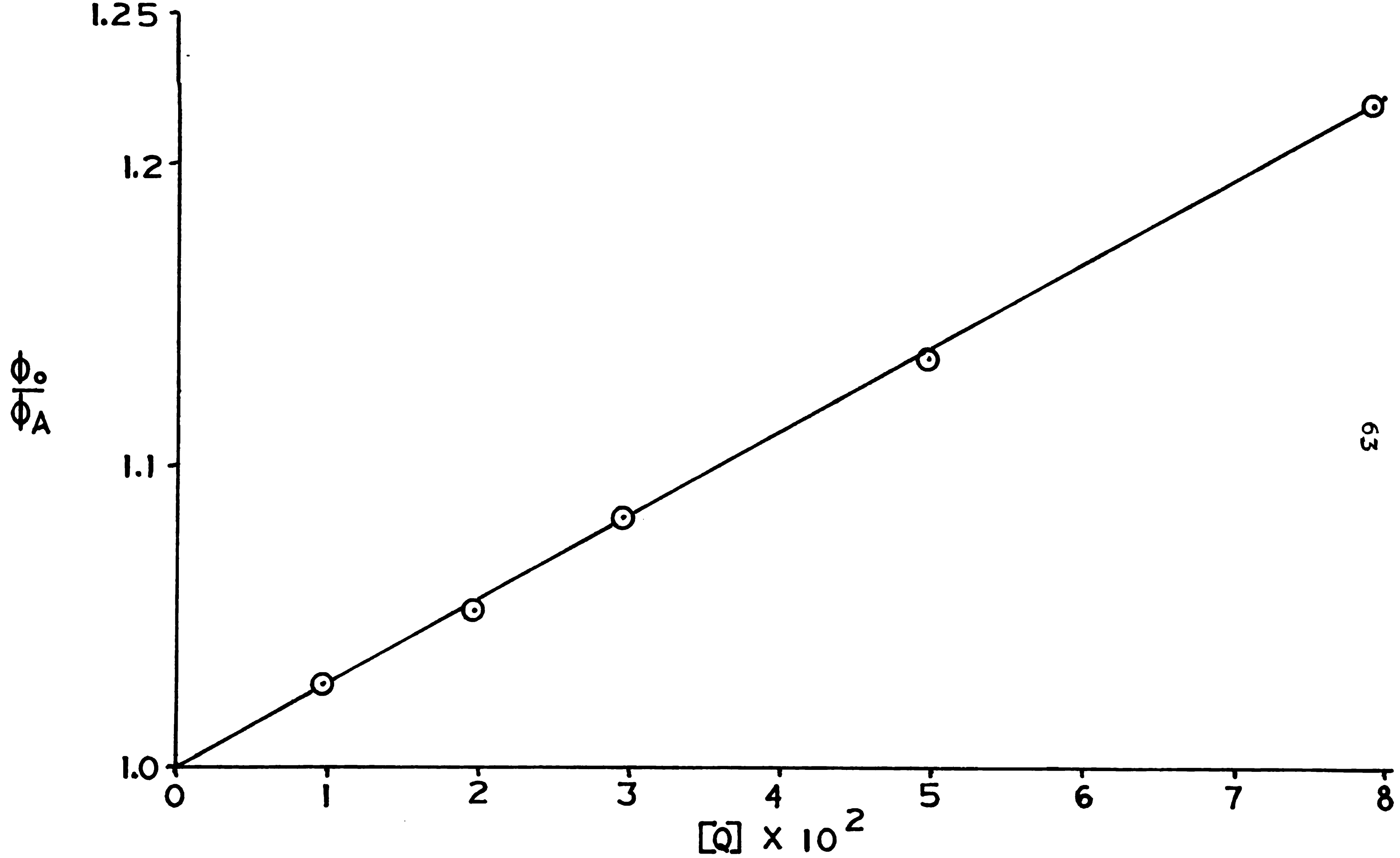
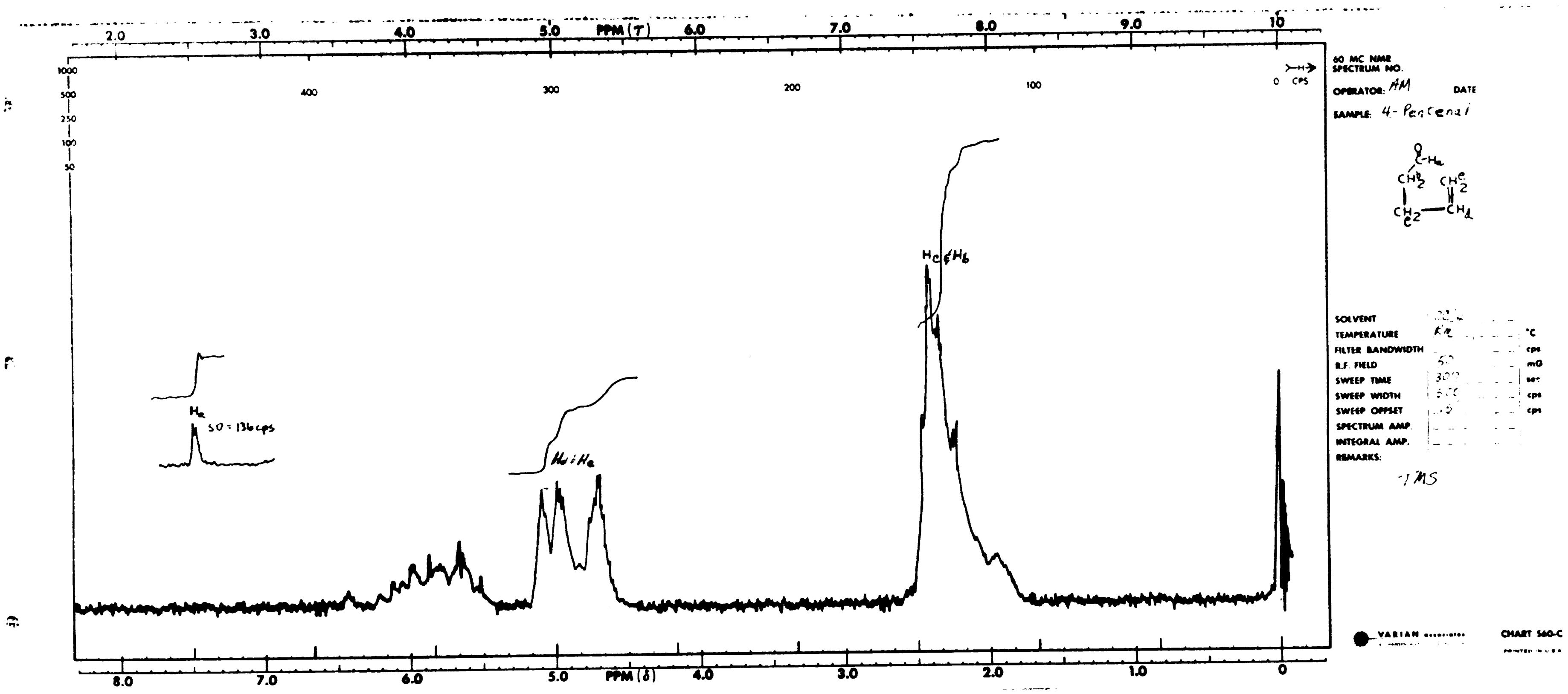


FIG. 10 STERN-VOLMER PLOT FOR QUENCHING OF 2,2-DIMETHYLCYCLOHEXANONE



60 MC NMR
SPECTRUM NO.
OPERATOR: AM DATE
SAMPLE: 4-Pentenal

SOLVENT [illegible]
TEMPERATURE RT °C
FILTER BANDWIDTH cps
R.F. FIELD 50 mG
SWEEP TIME 300 sec
SWEEP WIDTH 500 cps
SWEEP OFFSET [illegible] cps
SPECTRUM AMP.
INTEGRAL AMP.
REMARKS:
TMS

Fig. 11 NMR SPECTRUM OF 4-PENTENAL

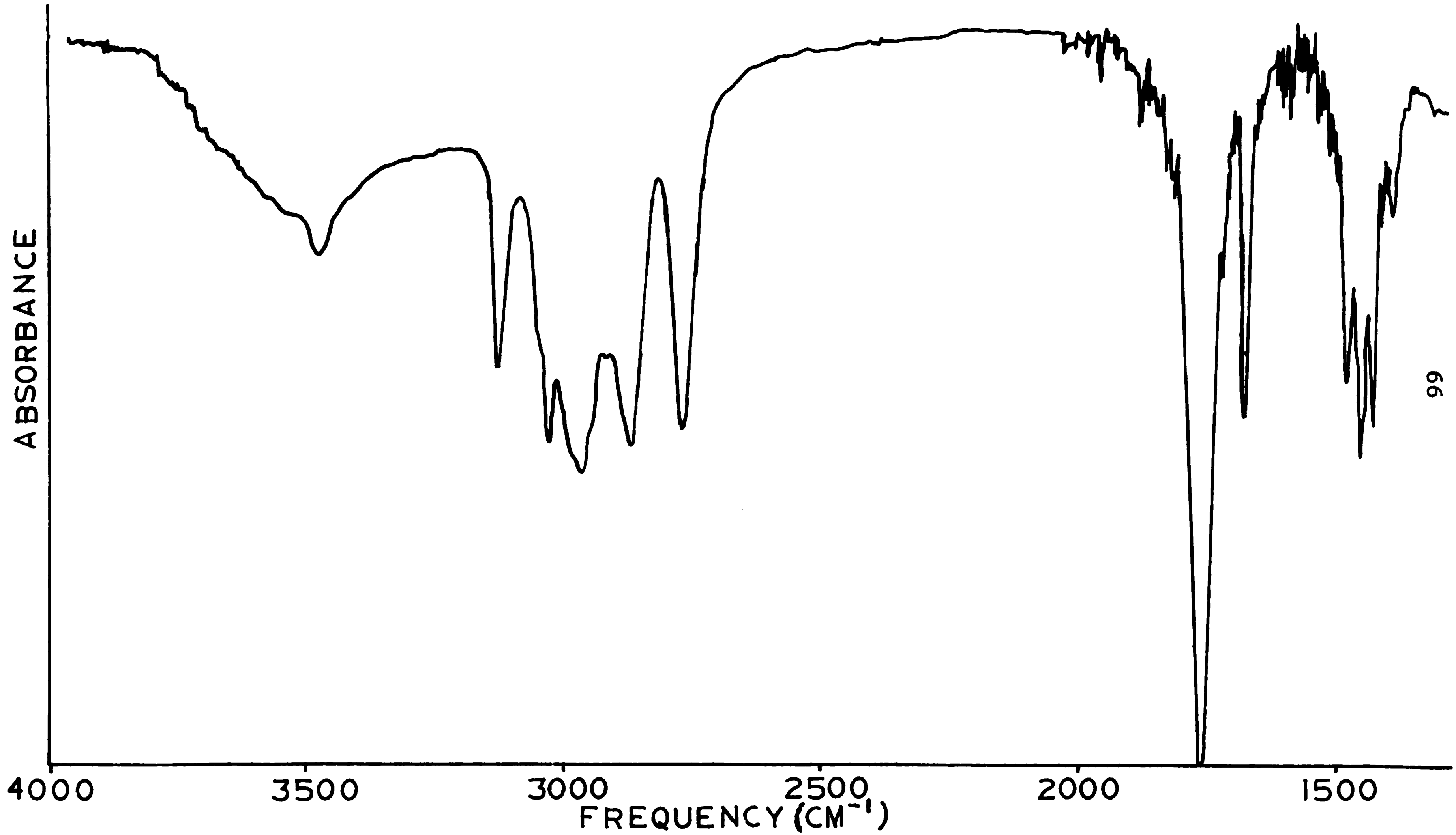


FIG. 12A IR SPECTRUM OF 4-PENTENAL (4000 - 1750 CM⁻¹)

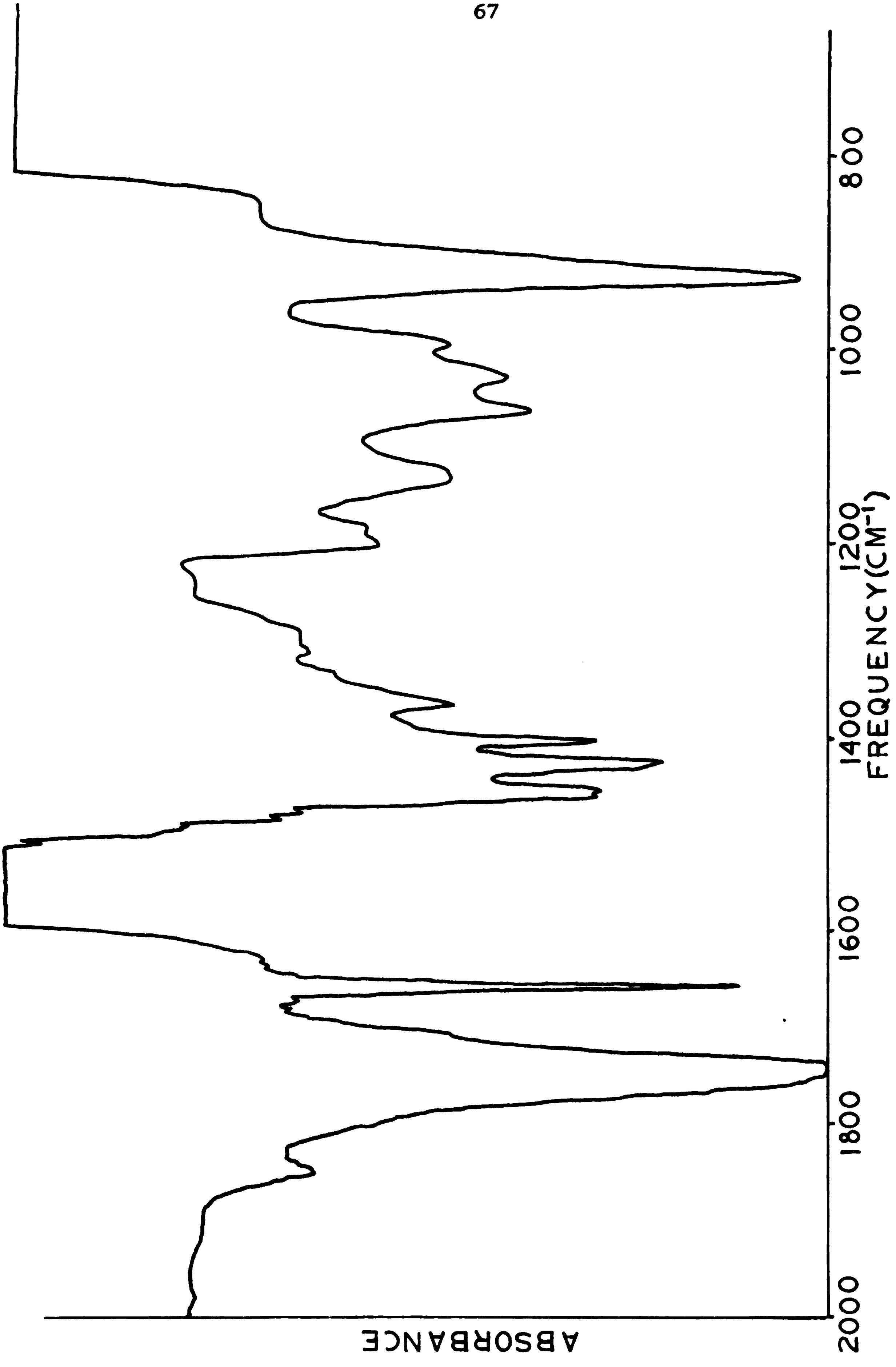


FIG. 12B IR SPECTRUM OF 4-PENTENAL (2000-800 CM^{-1})

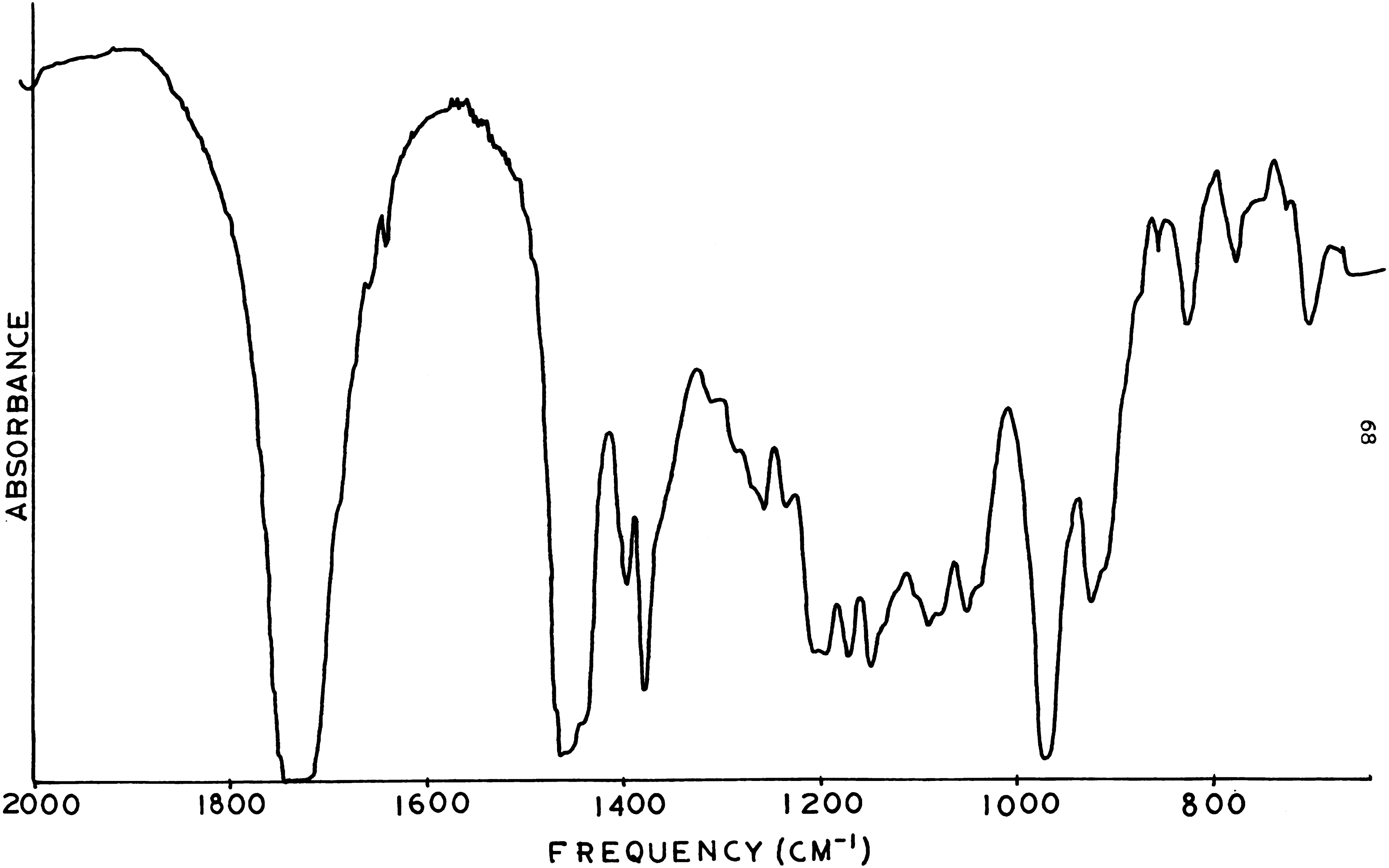


FIG. 13B IR SPECTRUM OF 2-METHYL-5-HEPTENAL (2000-800 CM^{-1})

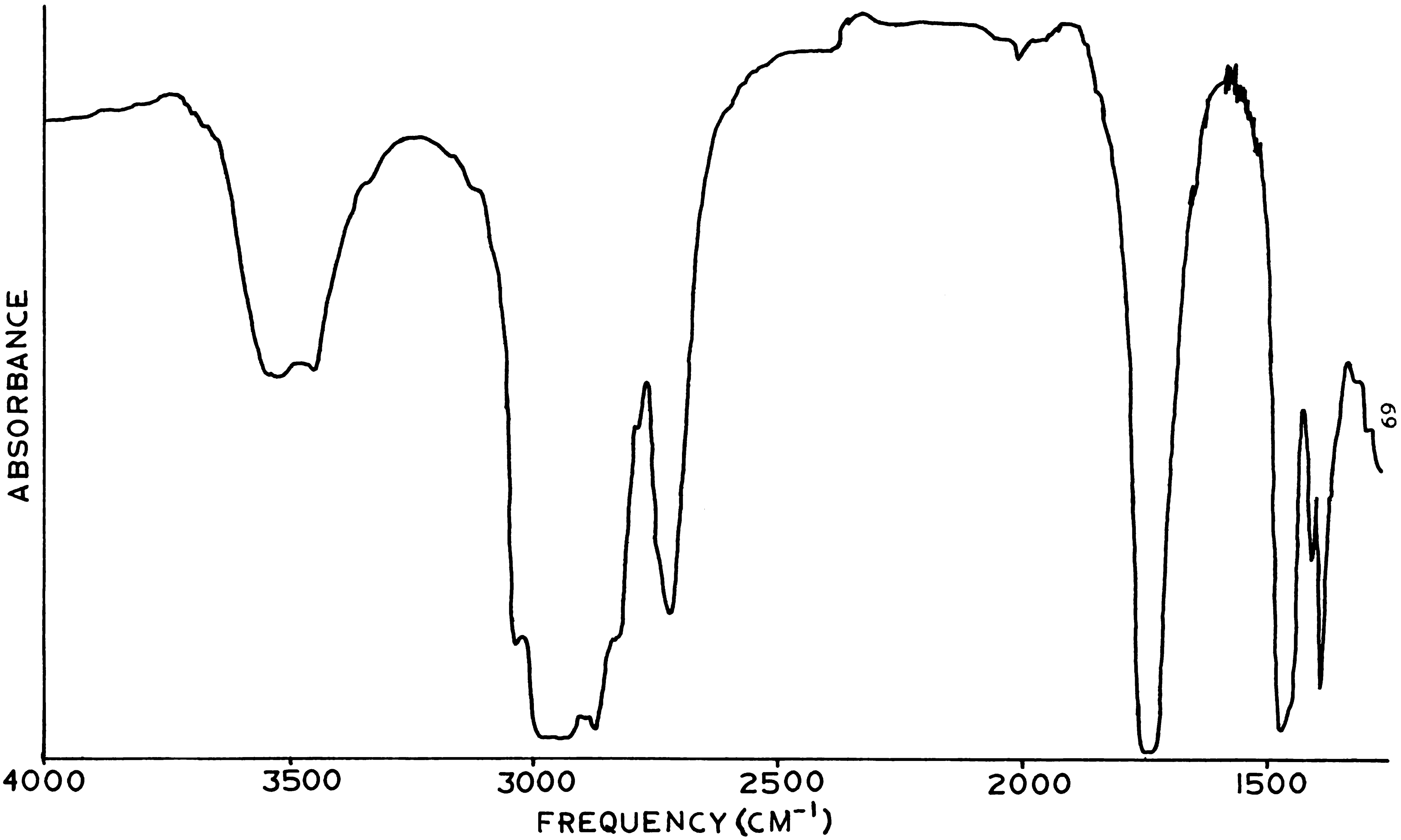


FIG. 13A IR SPECTRUM OF 2-METHYL-5-HEPTENAL (4000-1750 CM^{-1})

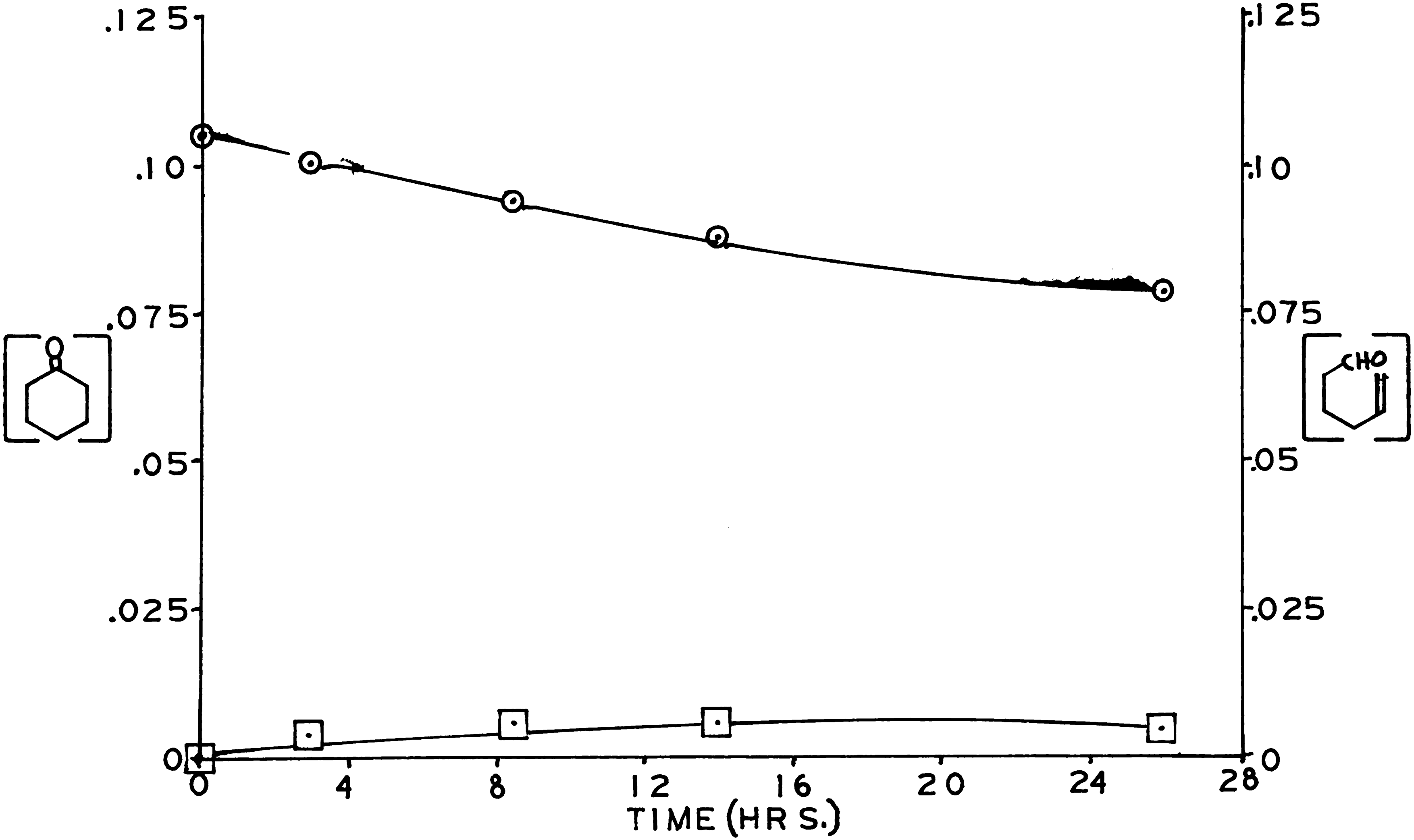


FIG.14 DISAPPEARANCE OF CYCLOHEXANONE VERSUS APPEARANCE OF 5-HEXENAL AS A FUNCTION OF TIME

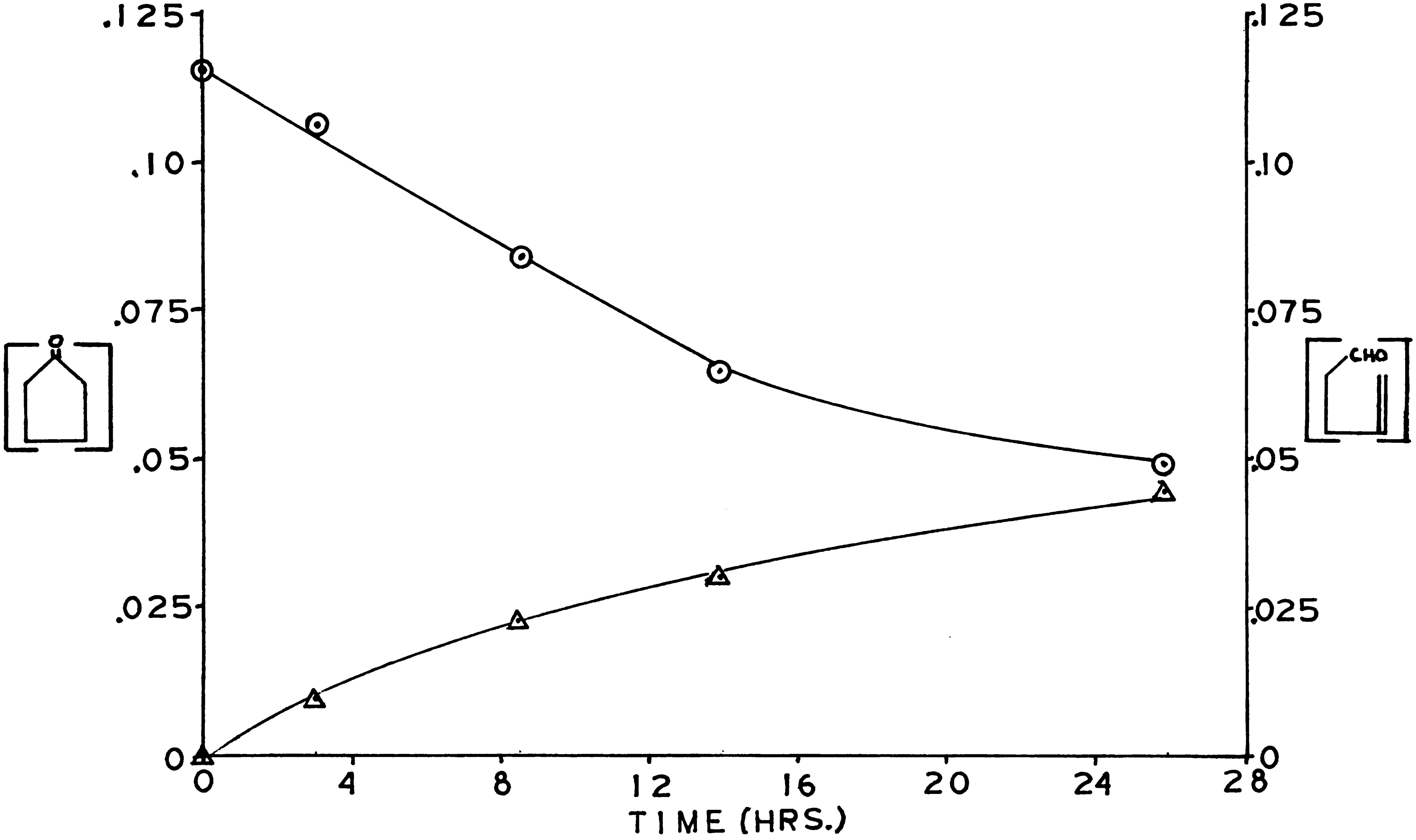


FIG.15 DISAPPEARANCE OF CYCLOPENTANONE VERSUS APPEARANCE OF 4-PENTENAL AS A FUNCTION OF TIME

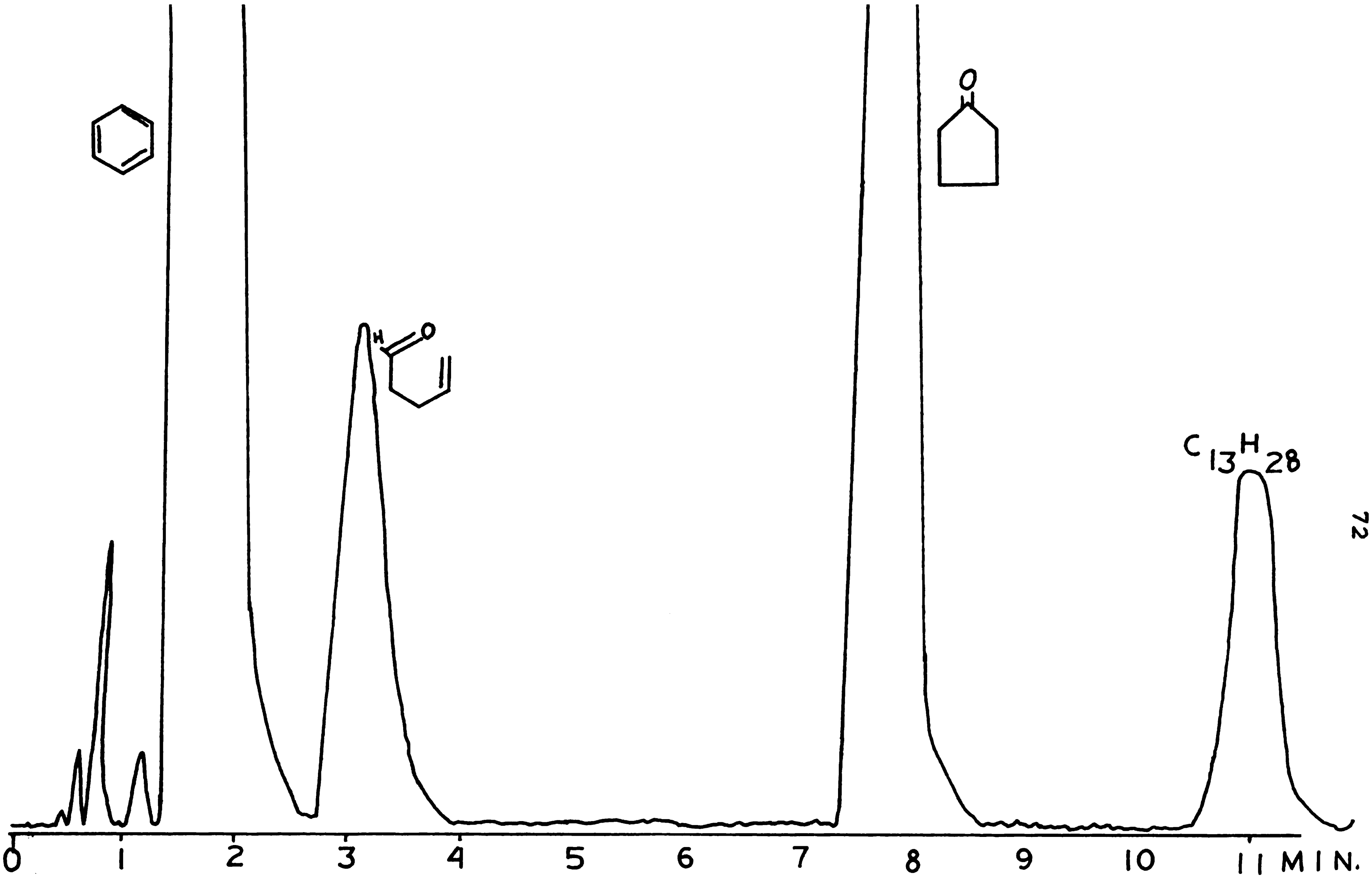


FIG. 16 VPC TRACE FOR CYCLOPENTANONE PHOTOLYZATE

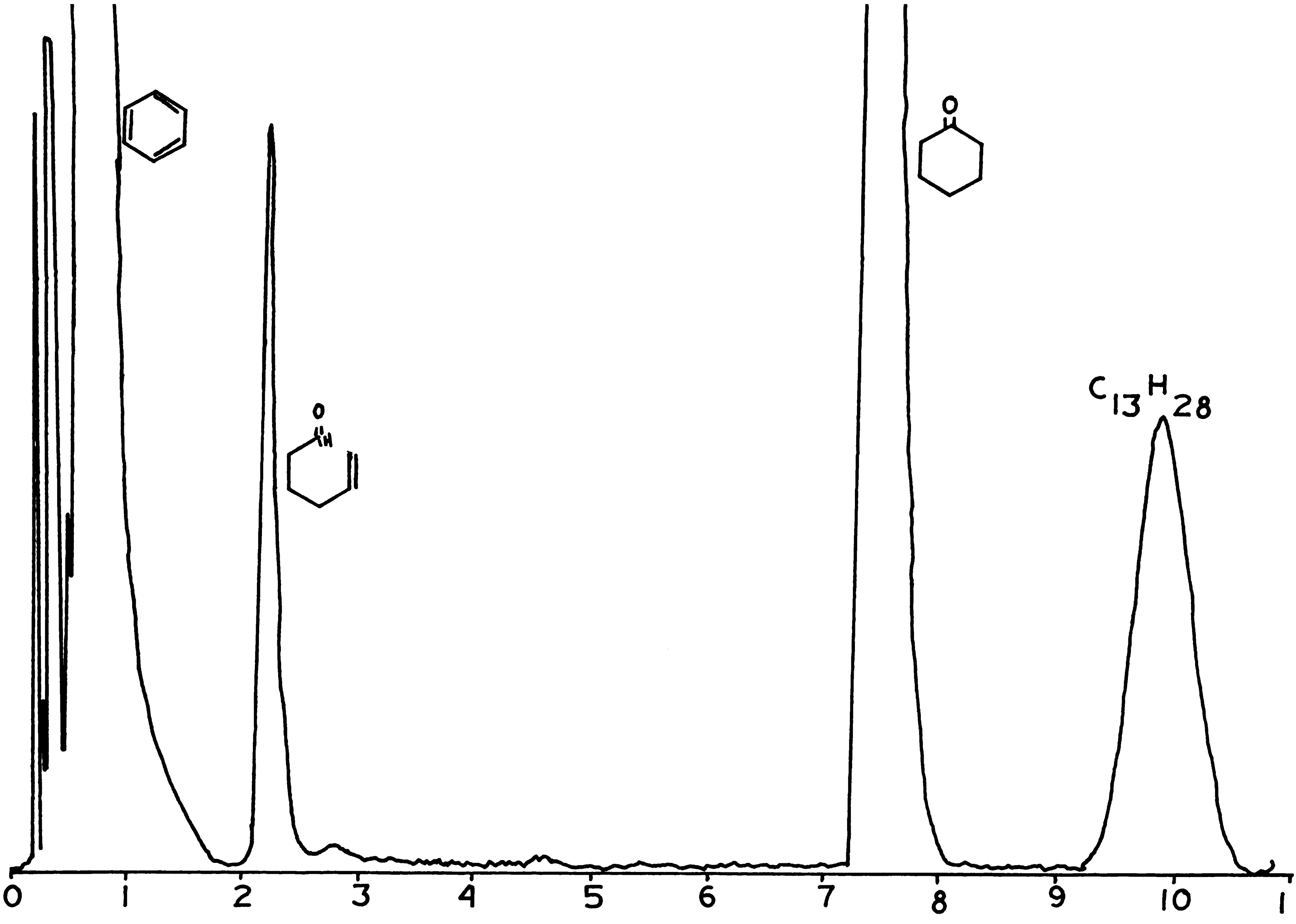


FIG.17 VPC TRACE FOR CYCLOHEXANONE PHOTOLYZATE

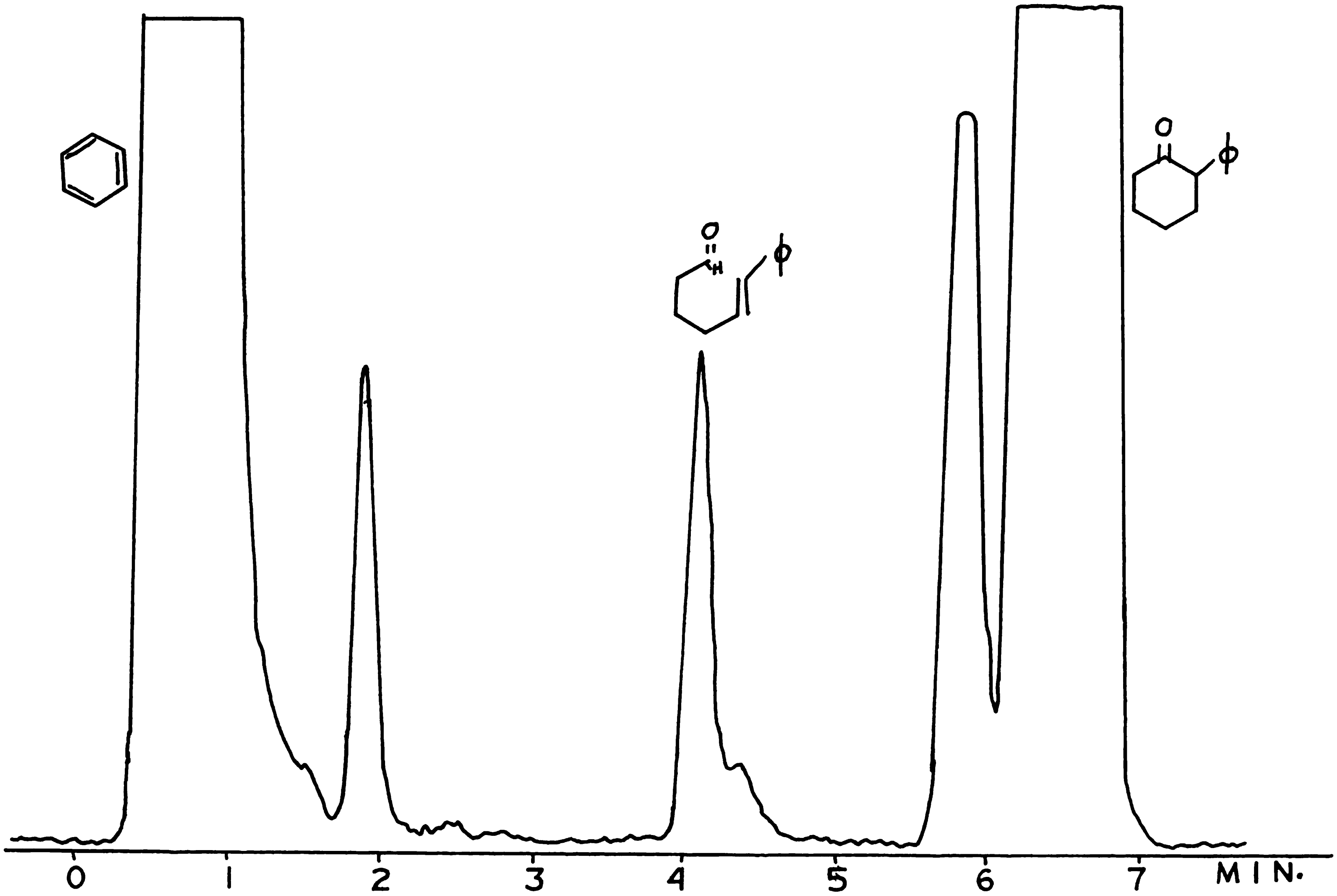


FIG.18 VPC TRACE FOR 2-PHENYLCYCLOHEXANONE PHOTOLYZATE

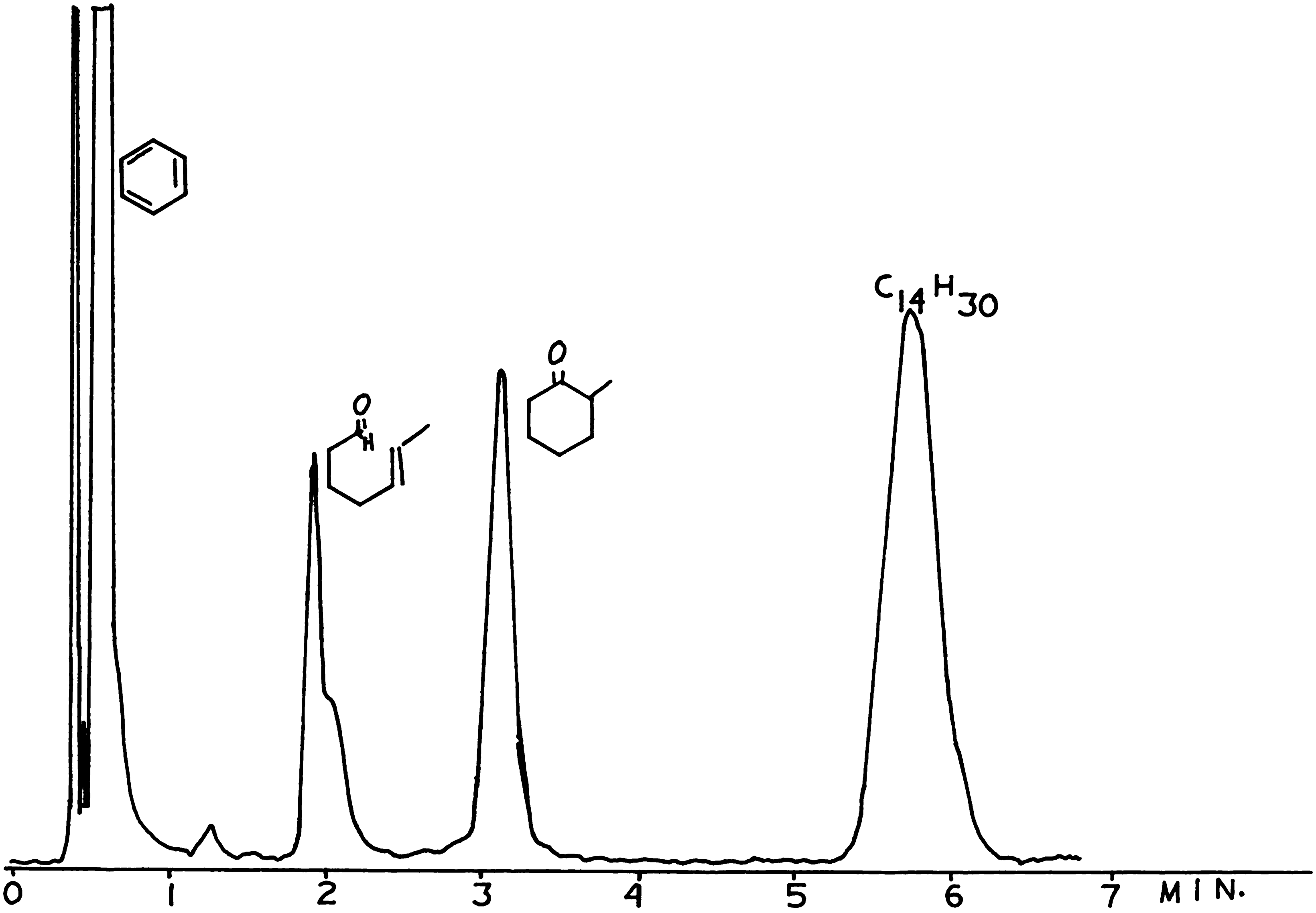


FIG. 19 VPC TRACE FOR 2-METHYLCYCLOHEXANONE PHOTOLYZATE

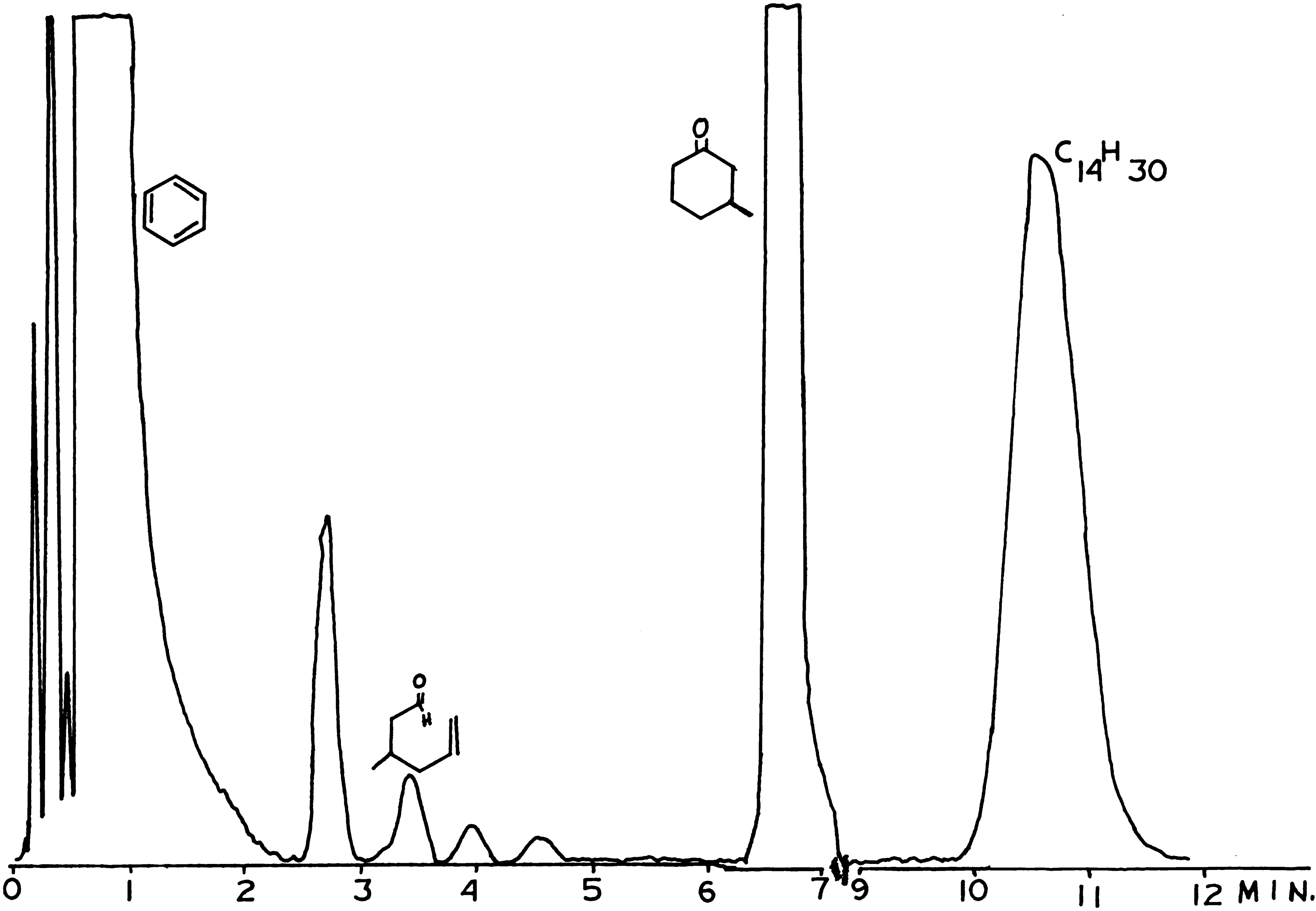


FIG. 20 VPC TRACE FOR 3-METHYLCYCLOHEXANONE PHOTOLYZATE

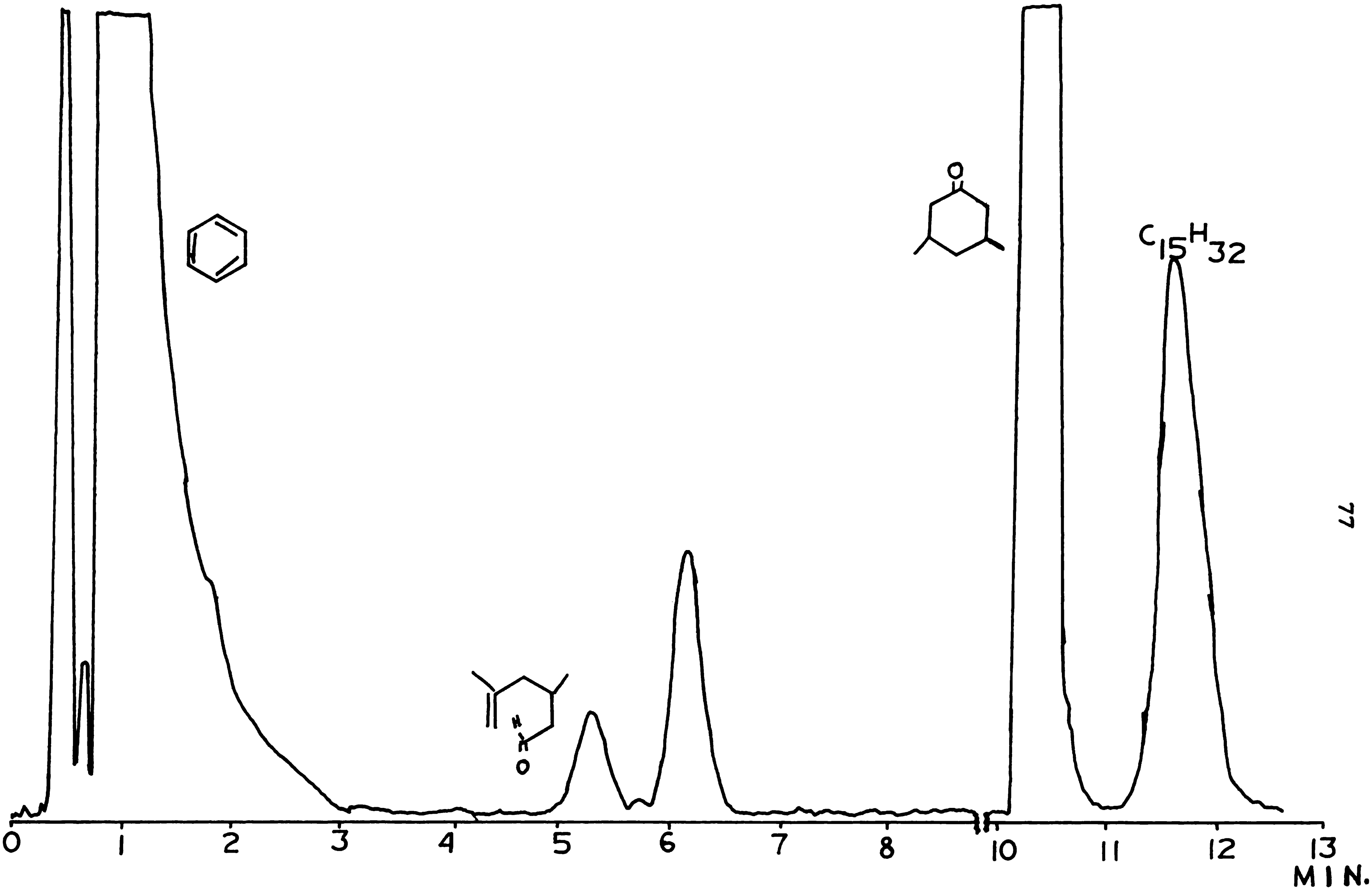


FIG. 21 VPC TRACE FOR 3,5-DIMETHYLCYCLOHEXANONE PHOTOLYZATE

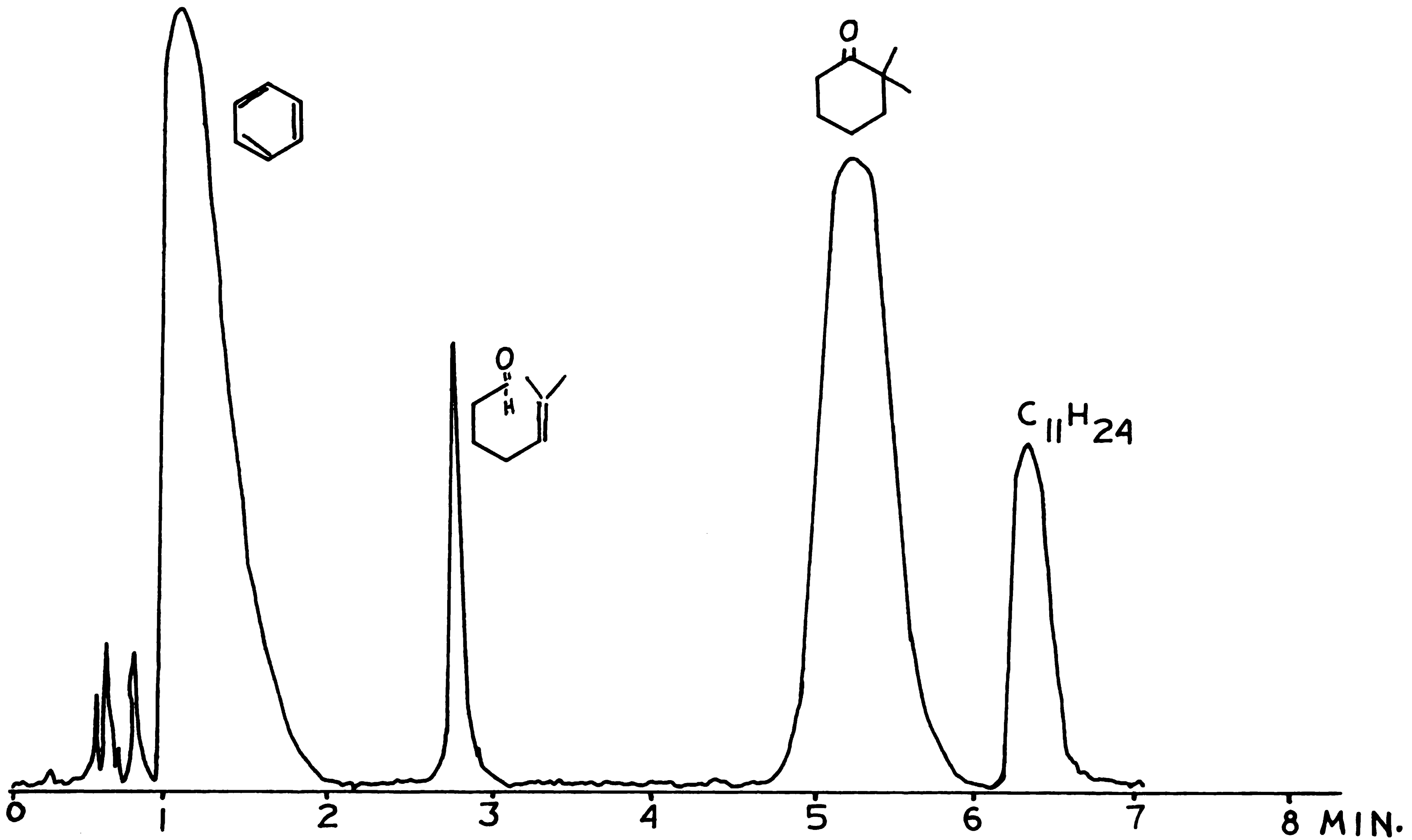


FIG. 22 VPC TRACE FOR 2,2-DIMETHYLCYCLOHEXANONE PHOTOLYZATE

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