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## ABSTRACT

### PART I

THE CRYSTAL AND MOLECULAR STRUCTURE OF DIBASKETENE

### PART II

THE REACTION OF ALLYL LITHIUM WITH STILBENE

BY

Neil Evan Jones

Photolysis of basketene, pentacyclo- $[4.4.0.0^2,5.0^3,8.0^4,7]$  dec-9-ene, yields a dimer which crystallizes in the space group  $P\bar{1}$  with  $Z = 1$ . It was necessary to use a combination of symbolic addition and Patterson methods to solve the structure of this compound. Dibasketene is a simple 2+2 cycloadduct which has the anti stereochemistry about the central four-membered ring.

### PART II

In an attempt to carry out a  $[2 + 3]$  anionic carbocycloaddition reaction, allyl lithium was reacted with stilbene. The product was 1-methyl-2,3,4,5-tetraphenylcyclohexane. Similarly,  $\beta$ -methallyl lithium gave 1,1-dimethyl-2,3,4,5-tetraphenylcyclohexane; and  $\alpha$ -methallyl lithium gave a small amount of cis-1,2-dimethyl-3,4,5,6-tetraphenylcyclohexane.

Neil Evan Jones

The structures of these compounds were assigned on the basis of their spectral properties; and, conversely, their structural similarity made possible a very detailed interpretation of their spectra.

A mechanism for the formation of these compounds, involving a series of 1,2 carbanion-olefin additions, is discussed.

PART I

THE CRYSTAL AND MOLECULAR STRUCTURE OF DIBASKETENE

PART II

THE REACTION OF ALLYL LITHIUM WITH STILBENE

By

Neil Evan Jones

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**To Frances**

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"...there is still some art left  
to crystal structure analysis..."

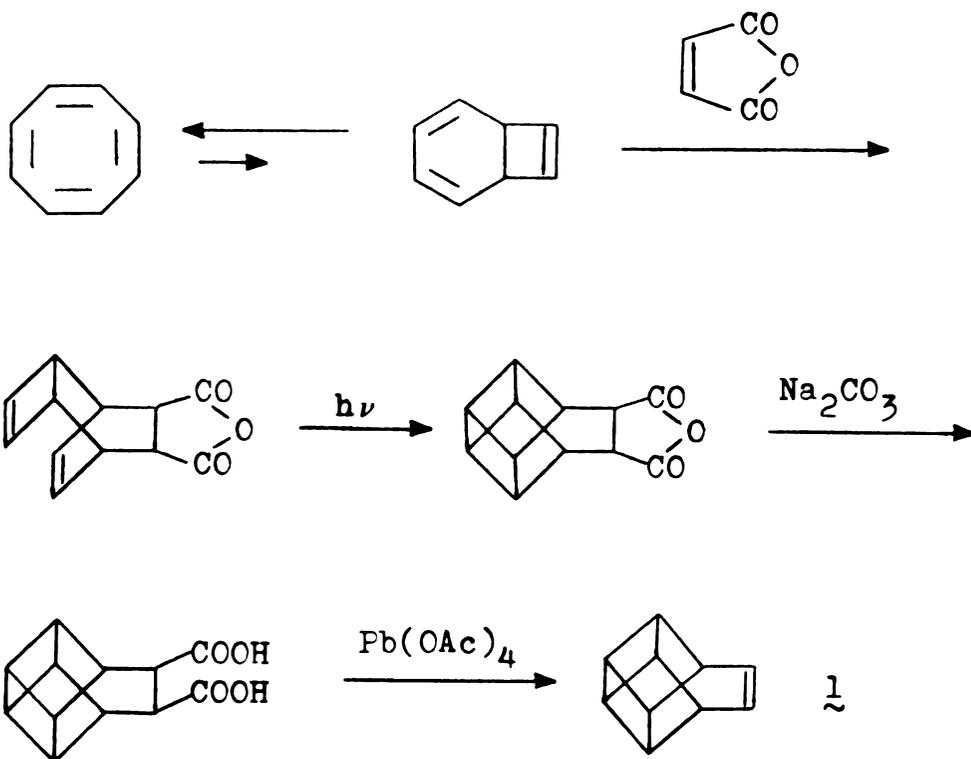
G.H. Stout and L.H. Jensen

Part I

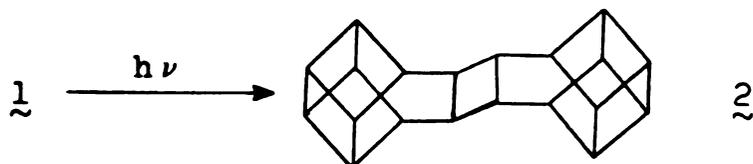
**The Crystal and Molecular Structure of Dibasketene**

## INTRODUCTION

The hydrocarbon basketene, 1, pentacyclo-  
 $[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]$  dec-9-ene, can be made from  
 cyclooctatetraene in an overall yield of 12% (1).

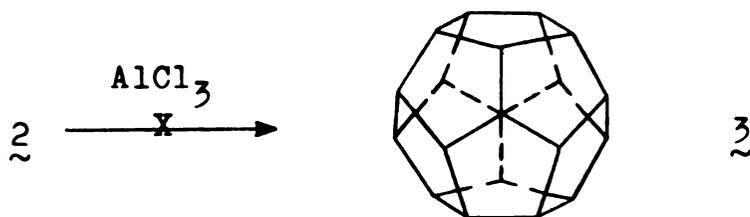


Photolysis of 1 produces dibasketene, 2 (2).



The dimeric nature of  $\underline{2}$  was established by mass spectrometry; but spectroscopic methods could neither rule out skeletal rearrangements during the photoreaction nor determine the stereochemistry of the photoproduct. A single-crystal X-ray diffraction study has resolved these questions.

It was hoped that  $\underline{2}$  would undergo a Lewis-acid catalyzed rearrangement to dodecahedrane,  $\underline{3}$ ; but all attempts to carry out this reaction have failed (2).



## EXPERIMENTAL

Clear, platelike crystals of dibasketene were grown by slow cooling of a hot, saturated xylene solution. Preliminary oscillation and Weissenberg photographs indicated triclinic symmetry. An irregularly shaped crystal of approximate dimensions 0.8 x 0.8 x 0.25 mm was mounted with a  $c^*$  axis coincident with the  $\phi$  axis of a quarter-circle single crystal orienter mounted on a General Electric XRD-5 manual diffractometer. Unit cell dimensions were calculated from a least-squares refinement of the setting angles of nine axial reflections that had been carefully determined using Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ):

$$\begin{array}{lll} a = 10.089(4) \text{ \AA} & \alpha = 115.20(5)^\circ & V = 312.3 \text{ \AA}^3 \\ & & \rho_{\text{calc'd}} = 1.38 \text{ g}\cdot\text{cm}^{-3} \\ b = 6.529(3) \text{ \AA} & \beta = 103.11(5)^\circ & \rho_{\text{obs'd}} = 1.36 \text{ g}\cdot\text{cm}^{-3} \\ & & Z = 1 \text{ molecule/cell} \\ c = 5.450(3) \text{ \AA} & \gamma = 76.33(5)^\circ & \mu = 5.82 \text{ cm}^{-1} \end{array}$$

The intensities of the 644 independent reflections within the sphere  $2\theta \leq 100^\circ$  ( $d_{\text{min}} \approx 1.0 \text{ \AA}$ ) were measured by the stationary crystal-stationary counter technique with balanced Ni-Co filters. A reflection was considered unobserved only if background counts exceeded peak

counts; and this occurred but once. During the data collection the intensities of three axial reflections were measured periodically to insure against errors from loss of alignment or deterioration of the diffraction pattern of the crystal due to X-ray exposure. The measured intensities were corrected for Lorentz and polarization effects and for absorption (3). The absorption correction was computed from the geometry of the crystal, the orientation of its faces with respect to the single-crystal orienter, and the value of its linear absorption coefficient,  $\mu$ ; and the values of the absorption correction factor ranged from 1.16 to 1.62. An absolute scale factor and an overall temperature factor were estimated by Wilson's method ( $B = 1.79 \text{ \AA}^2$ ); and from these structure factor magnitudes,  $|F|$ 's, and normalized structure factor magnitudes,  $|E|$ 's, were derived:

$$|E_{\vec{h}}| = \sqrt{U_{\vec{h}}^2 / U^2}$$

$$\text{where } |U_{\vec{h}}| = |F_{\vec{h}}| / \exp\left(\frac{-B \sin^2 \theta}{\lambda^2}\right) \sum_{i=1}^N f_i$$

and where  $f_i$  is the scattering factor of the  $i$ -th atom in the unit cell.

## SOLUTION OF THE STRUCTURE

### Symbolic Addition

The distribution of the  $|E|$ 's, shown in Table 1, established the centrosymmetry of the unit cell and, hence, of the molecule (4).

Table 1. Distribution of  $|E|$ 's.

	Experimental	Theoretical	
		Centric	Noncentric
Ave. $E^2$	1.000	1.000	1.000
Ave. $ E^2-1 $	0.954	0.968	0.736
Ave. $ E $	0.804	0.798	0.886
% $ E  \geq 1$	31.4	32.0	36.8
% $ E  \geq 2$	4.7	5.0	1.8
% $ E  \geq 3$	0.2	0.3	0.01

The symbolic addition method for direct sign determination (5) was applied to the 202 reflections whose  $|E|$ 's  $\geq 1.0$ . The origin of the unit cell was fixed by assigning positive signs to three linearly independent reflections; and the signs of four additional reflections were represented by symbols (Table 2).

Table 2. Starting signs and symbols.

h	k	l	E	Sign
6	-2	1	3.70	+
-8	1	2	2.47	+
7	-1	1	2.42	+
6	-1	0	2.33	a
-7	1	2	2.49	b
3	3	0	2.25	c
5	-1	1	2.37	d

The signs of the remaining 195 reflections were expressed in terms of these signs and symbols by means of the  $\Sigma_2$  formula

$$\text{sign of } E_{\vec{h}} \approx \text{sign of } \sum E_{\vec{k}} E_{\vec{h}-\vec{k}} \quad \text{Equation 1.}$$

each with a high certainty, C, of correctness,

$$C = \prod (P/(1-P)),$$

where

$$P = \frac{1}{2} + \frac{1}{2} \tanh(N^{-1/2} |E_{\vec{h}}| |E_{\vec{k}}| |E_{\vec{h}-\vec{k}}|)$$

and N is the number of nonhydrogen atoms in the unit cell.

Relationships among the signs and symbols, given by individual terms on the right side of Equation 1, are shown in Table 3.

Table 3. Symbol and sign relationships.

Implication	$\log_{10} C$
a = +	120.5
b = +	4.8
c = +	25.0
d = +	31.1
a = b	47.0
a = c	2.1
a = d	40.5
b = c	0.0
b = d	37.3
c = d	4.0
abc = +	0.5
abd = +	44.5
acd = +	3.4
bcd = +	0.0
abcd = +	0.4

The data in Table 3 clearly imply that  $a = b = d = +$ ,  $c \neq a$  or  $b$  or  $d$  and is therefore  $-$ ; and this combination gives a reasonable distribution of positive and negative signs to the 202  $|E|$ 's. Accordingly, an E map was computed with these signs.

### Wrong E map

The E map contained a large number of peaks, and the following approach was used to try to separate the real from the spurious:

- (a) The 24 strongest peaks in the asymmetric unit, of which a maximum of 10 could be real, were contoured.
- (b) For each of the 24  $x_i, y_i, z_i$  coordinates the values of the sharpened Patterson function at  $2x_i, 2y_i, 2z_i$  and at  $x_i - x_j, y_i - y_j, z_i - z_j$  etc. were computed. A total of five peaks were thus found to be consistent with the Patterson function in both inter- and all intramolecular vectors.
- (c) Of these five peaks, four appeared to form a part of the assumed molecular structure (Figure 1); and one was within a bonding distance of its mate at  $-x, -y, -z$ .

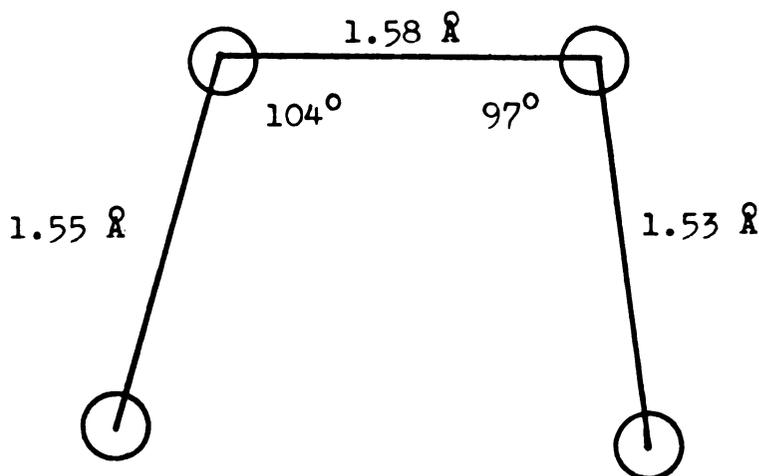


Figure 1. A molecular fragment to be compared with C(3)-C(8)-C(9)-C(10) in Figure 3.

(d) A structure factor calculation with the five peaks gave an R,

$$R = \frac{\sum \left| |F_o| - |F_c| \right|}{\sum |F_o|} \times 100\%,$$

of 60% but strongly contradicted the assumed sign of the symbol d.

(e) A Fourier synthesis based on the five peaks resurrected many of the doubtful peaks in the original **E** map and did not reveal a molecular structure.

(f) Fearing that one or more of the five peaks was spurious despite the rigorous selection process, three-dimensional atomic Patterson superpositions (6) were carried out at each using both the sum and minimum functions as a measure of agreement; but, again, no molecular structure was revealed.

At this point the original choice of signs was called seriously into question.

## Right E map

In order to obtain phase information independent of the symbolic addition method, the (hk0) Patterson projection, Figure 2, was examined. The overall appearance of this projection suggests that the molecule straddles the (110) plane.  $|F_{110}|$ , the largest  $|F|$ , should therefore be positive; and this is what Equation 1 indicated. Furthermore, the large peak at  $x = 0.04$ ,  $y = 0.22$  is the projection of the largest peak in the three-dimensional Patterson which occurs at  $z = 0.06$  and is ca.  $1.5 \text{ \AA}$  from the origin. If this peak is the coincidence of the vectors between the eight pairs of atoms which form zero-atom bridges spanning the mirror plane of dibasketene (see Figure 3), then the (110) plane is a good approximation to that mirror plane.

To test this hypothesis, a model of dibasketene was built on the same scale as the projection map, the assumption was made that the center of symmetry of the molecule lies at  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ ; and approximate x,y atomic coordinates were obtained by placing the model on top of the map. A calculation of the (hk0) structure factors gave an R of only 63%; but, of the 27 reflections whose  $|E|$ 's  $\geq 1.0$ , the 19 for which  $|F_c| \geq 2.0$  were all consistent only with the sign combination  $a = +$ ,  $b = c = d = -$ . An E map computed with this set of signs, which had many contradictions on the right side of Equation 1, contained only ten strong, sharp peaks and revealed the molecular structure on inspection.

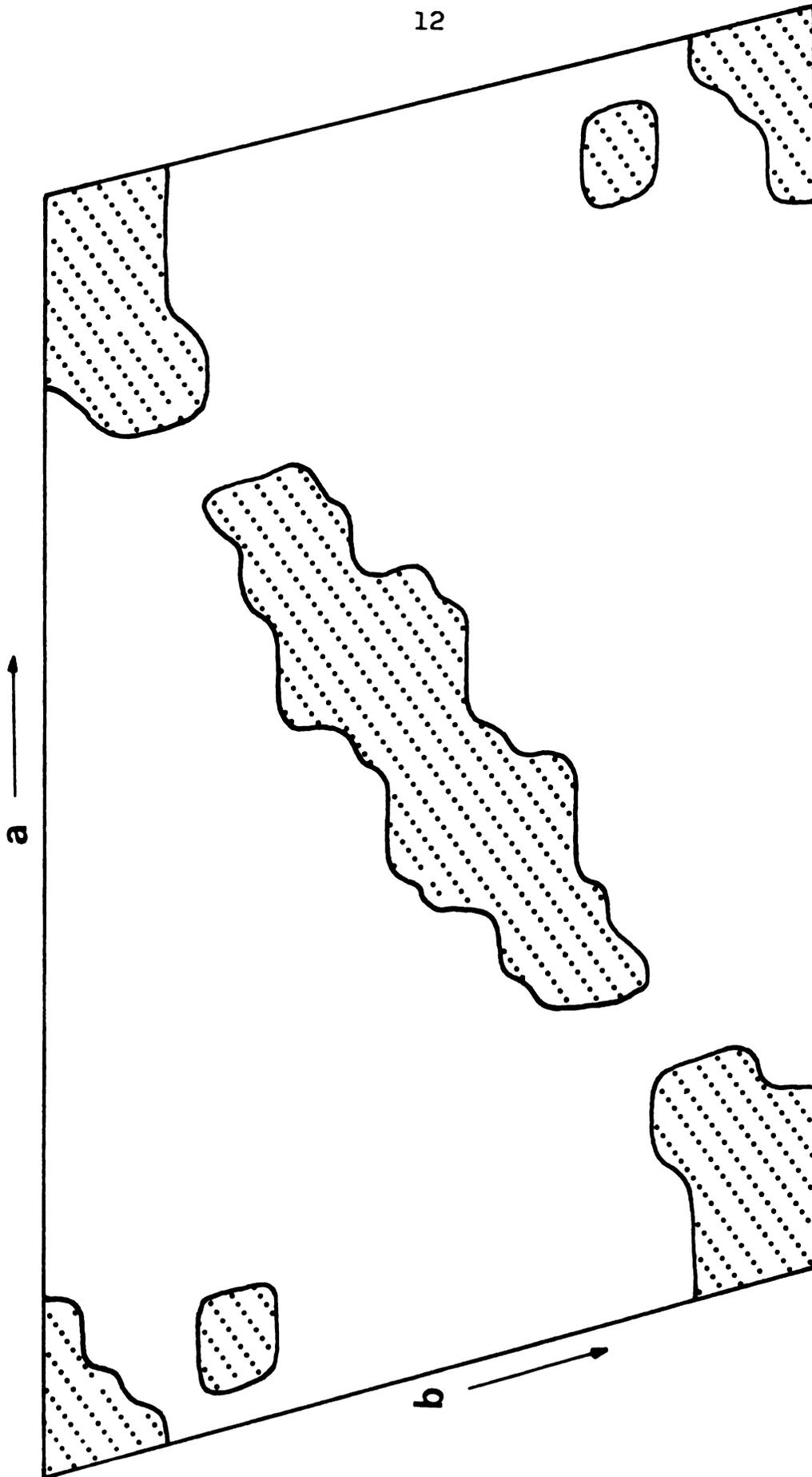


Figure 2. The (hk0) Patterson projection. Regions of high electron-squared density are shaded.

## Afterthoughts

There are two likely explanations for the fact that the correct sign combination was not the most self-consistent in terms of Equation 1.

(a) Equation 1 was derived on the assumption of a random distribution of scattering matter in the unit cell (7). This is clearly not the case with dibasketene: The molecule is very compact and has a mirror plane that is not part of the space group symmetry.

(b) In solving the structure of the alkaloid jamine (8), which crystallizes in the space group  $P\bar{1}$ , Karle and Karle also found a beguilingly self-consistent set of signs which synthesized recognizable molecular fragments in the wrong places in the unit cell. They had to compute and examine several  $E$  maps to find the correct one. They ascribed their difficulties to the fact that, with a triclinic crystal, the only relationship among the  $F$ 's that can be utilized in applying Equation 1 is  $F(hk\ell) = F(\bar{h}\bar{k}\bar{\ell})$ ; i.e., there are no direct indications that a given symbol is negative.

## REFINEMENT OF THE STRUCTURE

A Fourier synthesis with the observed structure factor amplitudes and the signs calculated from the atomic positions in the E map gave improved atomic coordinates. Full-matrix least squares refinement of the structure (9), beginning at R = 24.3%, was carried out in five stages.

(a) One cycle of unit-weight refinement of the coordinates, isotropic thermal parameters, and scale factor reduced R to 18.5%. The average B was reduced from 1.79 to 1.47 and the scale, from 1.0 to 0.9. To determine the reason for the direction and magnitude of these changes, a difference map was computed; and the positions of nine of the ten hydrogen atoms were revealed.

(b) The scale factor and the individual B's were returned to their original values, and a structure factor calculation including the hydrogen atoms gave an R of 15.7%. At this point a weighting scheme was decided upon.

$$w(|F_o|) = 1/\sigma^2(|F_o|)$$

where

$$\sigma(|F_o|) = \frac{|F_o| \sum_{i=1}^N \left| |F_o|_i - |F_c|_i \right|}{N} \quad \text{Equation 2.}$$

N

and where  $N$  is the number of  $|F_o|_i$ 's between  $|F_o|$  and  $|F_o| + 1.0$  and  $F_c = F$  calculated at  $R = 15.7\%$ . Zero weight was given to six strong, low-angle reflections which showed severe secondary extinction and to reflections whose  $|F_o| \leq 1.0$ . Three cycles of refinement of the scale and the carbon-atom parameters, in the presence of the hydrogen atoms, reduced  $R$  to  $12.7\%$ .

(c) The six reflections showing extinction were corrected by means of a Darwin plot; and two more cycles of refinement reduced  $R$  to  $10.3\%$ .

(d) A second difference map was computed and the remaining hydrogen atom found. A final cycle of isotropic refinement reduced  $R$  to  $10.1\%$ .

(e) Two cycles of refinement with anisotropic thermal parameters for carbon reduced  $R$  to a final value of  $9.1\%$ . At this point parameter shifts were less than  $10\%$  of their esd's. The  $R$  factor, omitting the weak, zero-weight reflections, is  $8.6\%$ . An  $R$  factor of  $5-8\%$  is considered reasonable for structures determined by comparable methods. In the case of dibasketene the rather high value of the final  $R$  is probably due largely to poor alignment and centering of the crystal during the data collection.

The anisotropic refinement reduced the weighted  $R$  factor from  $13.7\%$  to  $12.3\%$ . Given the increase in the number of parameters, this improvement is significant, according to Hamilton's  $R$ -ratio test (10), at the  $0.005$

level assuming that all errors are random.

A correlation coefficient is a measure of the interdependence of two parameters. If it is large, simultaneous least-squares refinement of the parameters may be slow or may give incorrect results. Correlation coefficients between atomic positional parameters are generally less than 0.2 but will be greater than this when unit cell angles are significantly different from  $90^\circ$  and when the atoms are related by crystallographic symmetry or pseudo-symmetry (11). Because the angle  $\alpha$  in dibasketene is  $115^\circ$ , the correlation coefficients between the y and z coordinates of individual carbon atoms were disturbingly high, ca. 0.4; but this did not prove to be an obstacle to smooth refinement of the structure.

The variance of a unit-weight reflection is given by the formula

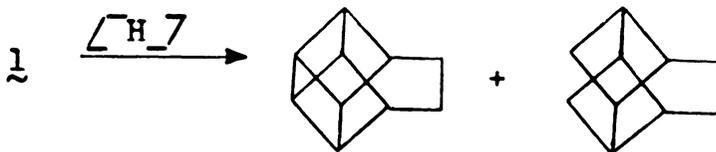
$$V = \sqrt{\frac{\sum w(F_o - F_c)^2}{D.F.}}$$

where D.F., the number of degrees of freedom, is equal to the number of reflections minus the number of parameters describing the structure. If V is significantly greater than 1.0, the weighting scheme underestimates the average error in the structure factors. For dibasketene  $V = 1.00$ . This is reasonable since the weighting scheme, Equation 2, is based upon the average differences in the calculated and observed structure factors.

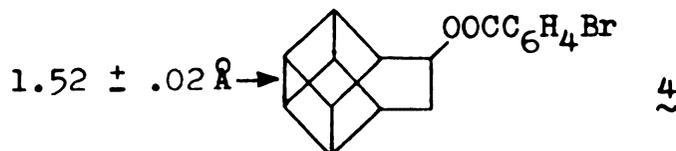
## RESULTS AND DISCUSSION

The molecular geometry of dibasketene is shown in Figure 3. The important interatomic distances and bond angles are given in Table 4. Table 5 gives the final atomic parameters; and Table 6 lists the calculated and observed structure factors.

The average carbon-carbon bond length in dibasketene is 1.55 Å; and the average carbon-hydrogen length is 1.07 Å, exactly the values found for cubane (12). The information in Table 4 relating to C(6) and C(7) is consistently anomalous and suggests that there is decreased p-character in the sigma bonds formed by these two atoms. It is an experimental fact (1) that when the double bond in basketene itself is hydrogenated, the reaction is complicated by the hydrogenolysis of the bond corresponding to C(6)-C(7).



The accuracy of the value of 1.52 Å for the C(6)-C(7) bond length is confirmed by the reported structure of basketane-9-ol p-bromobenzoate, 4 (13).



This value is closer to the carbon-carbon bond length in cyclopropane,  $1.524 \pm 0.014 \text{ \AA}$  (14), than to that in cyclobutane,  $1.548 \pm 0.003 \text{ \AA}$  (15).

In Table 7 the (110) plane is compared with the mirror plane of the molecule, taken as the least-squares plane of the midpoints between the mirrored atoms. The deviations of the midpoints from this plane are insignificant at the 95% level (16). Moreover, as shown in Table 8, there is no significant difference in the arrangements of the crystallographically nonequivalent atoms on opposite sides of the mirror plane of the molecule. The negligible correlation coefficients found between the corresponding coordinates of the mirrored atoms during refinement of the structure prove that there is no true crystallographic mirror plane in the unit cell and that the space group is indeed  $P\bar{1}$ .

Finally, the interatomic distances and bond angles in dibasketene are compared in Table 4 with the corresponding values reported for 4. There are no significant differences between the two structures (see Table 8).



**Table 4.** Interatomic distances and bond angles and their average esd's.

Distances			Angles		
C(1)-C(2)	1.56 $\text{\AA}$		C(2) -C(1) -C(12)	89.9 $^{\circ}$	
C(1)-C(12)	1.54	(1.58) <sup>a</sup>	C(2) -C(1) -C(20)	115.3	
C(1)-C(20)	1.53	(1.51)	C(12)-C(1) -C(20)	111.7	(112) <sup>a</sup>
C(2)-C(3)	1.53	(1.51)	C(1) -C(2) -C(3)	115.6	
C(3)-C(4)	1.54	(1.52)	C(1) -C(2) -C(11)	90.1	
C(3)-C(8)	1.55	(1.52)	C(3) -C(2) -C(11)	112.1	(112)
C(4)-C(5)	1.55	(1.57)	C(2) -C(3) -C(4)	116.9	(117)
C(4)-C(7)	1.57	(1.55)	C(2) -C(3) -C(8)	116.5	(117)
C(5)-C(6)	1.56	(1.55)	C(4) -C(3) -C(8)	86.8	(86)
C(5)-C(10)	1.55	(1.52)	C(3) -C(4) -C(5)	111.6	(112)
C(6)-C(7)	1.52	(1.52)	C(3) -C(4) -C(7)	90.2	(90)
C(6)-C(9)	1.57	(1.55)	C(5) -C(4) -C(7)	89.4	(89)
C(7)-C(8)	1.57	(1.55)	C(4) -C(5) -C(6)	89.5	(89)
C(8)-C(9)	1.55	(1.57)	C(4) -C(5) -C(10)	111.1	(112)
C(9)-C(10)	1.54	(1.52)	C(6) -C(5) -C(10)	90.2	(90)
C(3)-C(10)	2.68	(2.65)	C(5) -C(6) -C(7)	90.9	(91)
esd	0.01 $\text{\AA}$	(0.02)	C(5) -C(6) -C(9)	85.1	(85)
			C(7) -C(6) -C(9)	90.5	(91)
			C(4) -C(7) -C(6)	90.2	(91)
			C(4) -C(7) -C(8)	85.3	(85)
			C(6) -C(7) -C(8)	90.6	(91)
			C(3) -C(8) -C(7)	89.9	(90)
			C(3) -C(8) -C(9)	110.6	(112)
			C(7) -C(8) -C(9)	89.4	(89)
			C(6) -C(9) -C(8)	89.5	(89)
			C(6) -C(9) -C(10)	90.5	(90)
			C(8) -C(9) -C(10)	112.1	(112)
			C(5) -C(10)-C(9)	86.4	(86)
			C(5) -C(10)-C(11)	117.2	(117)
			C(9) -C(10)-C(11)	116.2	(117)
			esd	0.5 $^{\circ}$	(1)

Table 4 (cont'd.)

C(1) -H(1)	1.15 <sup>a</sup>	C(2) -C(1) -H(1)	114 <sup>o</sup>
C(2) -H(2)	1.09	C(12)-C(1) -H(1)	121
C(3) -H(3)	1.04	C(20)-C(1) -H(1)	105
C(4) -H(4)	1.07	C(1) -C(2) -H(2)	109
C(5) -H(5)	1.11	C(3) -C(2) -H(2)	111
C(6) -H(6)	0.95	C(11)-C(2) -H(2)	118
C(7) -H(7)	0.97	C(2) -C(3) -H(3)	111
C(8) -H(8)	1.08	C(4) -C(3) -H(3)	116
C(9) -H(9)	1.19	C(8) -C(3) -H(3)	107
C(10)-H(10)	1.05	C(3) -C(4) -H(4)	122
esd	0.09 <sup>a</sup>	C(5) -C(4) -H(4)	116
		C(7) -C(4) -H(4)	121
		C(4) -C(5) -H(5)	111
		C(6) -C(5) -H(5)	126
		C(10)-C(5) -H(5)	123
		C(5) -C(6) -H(6)	113
		C(7) -C(6) -H(6)	135
		C(9) -C(6) -H(6)	127
		C(4) -C(7) -H(7)	126
		C(6) -C(7) -H(7)	135
		C(8) -C(7) -H(7)	115
		C(3) -C(8) -H(8)	124
		C(7) -C(8) -H(8)	123
		C(9) -C(8) -H(8)	114
		C(6) -C(9) -H(9)	124
		C(8) -C(9) -H(9)	109
		C(10)-C(9) -H(9)	126
		C(5) -C(10)-H(10)	110
		C(9) -C(10)-H(10)	119
		C(11)-C(10)-H(10)	107
		esd	5 <sup>o</sup>

<sup>a</sup>The value of the corresponding distance or angle in Å.



Table 5. Atomic parameters and their average esd's.

During refinement the esd's of the hydrogen-atom coordinates were set equal to 15 times those of the corresponding carbon-atom coordinates, and the  $\beta$ 's of the hydrogen atoms were set equal to those of the carbon atoms to which they are bonded; but no hydrogen-atom parameters were refined. The temperature factor expression used was  $\exp(-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl))$ . The  $\beta$ 's have been multiplied by  $10^4$ . The isotropic B's are in units of  $\text{\AA}^2$ ; and the peak heights,  $\rho$ 's, are in units of electrons/ $\text{\AA}^3$ .

Atom	x/a	y/b	z/c	$\beta$						B(i)			H(i)		
				$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	B(1)	B(2)	$\rho$ (1)	x/a	y/b	z/c
C(1)	0.4101	0.4226	0.3685	51	211	201	-20	10	112	2.02	7.56	0.398	0.293	0.145	
C(2)	0.5383	0.3507	0.5537	53	155	185	-18	9	88	1.88	7.40	0.503	0.326	0.713	
C(3)	0.6392	0.1420	0.4034	38	171	282	-31	-3	112	2.08	7.35	0.609	-0.010	0.373	
C(4)	0.6898	0.1442	0.1579	66	211	197	-1	33	65	2.46	7.40	0.640	0.068	-0.047	
C(5)	0.7425	0.3718	0.2331	65	262	224	-12	34	119	2.58	7.27	0.712	0.430	0.062	
C(6)	0.8903	0.2623	0.3248	65	254	317	-17	55	126	2.89	6.72	0.962	0.305	0.277	
C(7)	0.8396	0.0383	0.2511	61	227	326	16	39	103	2.91	6.72	0.880	-0.123	0.181	
C(8)	0.7923	0.1327	0.5400	73	206	226	-22	4	98	2.48	6.77	0.835	0.055	0.686	
C(9)	0.8432	0.3617	0.6147	50	214	266	-20	10	115	2.36	7.01	0.920	0.404	0.824	
C(10)	0.7292	0.5359	0.5357	46	163	176	-22	18	53	1.84	7.55	0.751	0.698	0.575	
esd	0.0005	0.0009	0.0011	7	20	27	9	11	19	0.11	----	0.008	0.014	0.016	

Table 6. Calculated and observed structure factors.

The structure factors are on an absolute scale in units of electrons;  $F_{000} = 140$  electrons.

M	K	L	F <sub>000</sub>	FCAL	M	K	L	F <sub>000</sub>	FCAL	M	K	L	F <sub>000</sub>	FCAL	M	K	L	F <sub>000</sub>	FCAL	M	K	L	F <sub>000</sub>	FCAL	M	K	L	F <sub>000</sub>	FCAL	M	K	L	F <sub>000</sub>	FCAL
0	0	1	46.1	-47.6	1	-5	3	10.6	-9.9	4	1	0	15.0	-13.1	7	0	2	1.5	-1.0	7	0	2	1.5	-1.0	7	0	2	1.5	-1.0					
0	0	2	2.2	-1.2	1	-5	4	1.4	-1.8	4	1	1	10.2	9.8	7	1	0	5.4	-6.3	7	1	0	5.4	-6.3	7	1	0	5.4	-6.3					
0	0	3	4.3	-3.3	1	-6	1	4.8	4.5	4	1	2	8.2	-7.0	7	1	1	8.9	8.0	7	1	1	8.9	8.0	7	1	1	8.9	8.0					
0	0	4	1.8	-1.2	1	-6	2	2.5	1.9	4	1	3	9.2	-9.0	7	1	2	2.1	-1.9	7	1	2	2.1	-1.9	7	1	2	2.1	-1.9					
0	1	0	8.8	-9.4	2	0	0	32.5	-29.5	4	2	0	6.5	6.3	7	2	0	5.5	4.1	7	2	0	5.5	4.1	7	2	0	5.5	4.1					
0	1	1	5.4	-5.6	2	0	1	10.2	9.4	4	2	1	2.9	-2.5	7	2	1	8.7	7.7	7	2	1	8.7	7.7	7	2	1	8.7	7.7					
0	1	2	7.3	-7.5	2	0	2	1.3	-1.3	4	2	2	2.3	1.9	7	2	2	10.2	-9.3	7	2	2	10.2	-9.3	7	2	2	10.2	-9.3					
0	1	3	2.9	2.8	2	0	3	1.7	1.1	4	2	3	2.2	-1.7	7	3	0	11.1	12.8	7	3	0	11.1	12.8	7	3	0	11.1	12.8					
0	1	4	4.4	-1.4	2	0	4	1.4	1.0	4	2	4	0	-3.4	7	3	1	13.3	-13.8	7	3	1	13.3	-13.8	7	3	1	13.3	-13.8					
0	2	0	4.0	-2.8	2	1	1	1.1	-1.8	4	3	1	7.3	-6.9	7	4	0	7.0	-11.8	7	4	0	7.0	-11.8	7	4	0	7.0	-11.8					
0	2	1	4.0	-4.2	2	1	1	1.1	-1.8	4	3	2	7.3	-6.9	7	4	1	13.7	-11.2	7	4	1	13.7	-11.2	7	4	1	13.7	-11.2					
0	2	2	2.7	2.0	2	1	2	7.9	7.0	4	4	0	8.3	-7.2	7	4	1	15.7	15.0	7	4	1	15.7	15.0	7	4	1	15.7	15.0					
0	2	3	5.8	-5.8	2	1	3	2.9	-2.5	4	4	1	6.7	-6.2	7	4	2	8.7	-8.4	7	4	2	8.7	-8.4	7	4	2	8.7	-8.4					
0	3	0	2.5	2.4	2	1	4	1.0	1.3	4	5	0	1.2	-.2	7	4	3	5.4	-6.8	7	4	3	5.4	-6.8	7	4	3	5.4	-6.8					
0	3	1	4.3	-3.2	2	2	0	22.0	-25.7	4	-1	1	16.6	-13.8	7	-2	2	1.4	3.8	7	-2	2	1.4	3.8	7	-2	2	1.4	3.8					
0	3	2	7.7	-7.0	2	2	1	8.7	8.4	4	-1	2	22.1	-19.4	7	-3	1	1.2	-1.0	7	-3	1	1.2	-1.0	7	-3	1	1.2	-1.0					
0	3	3	5.0	5.0	2	2	2	1.3	1.8	4	-1	3	-.4	-.2	8	0	0	3.0	2.5	8	0	0	3.0	2.5	8	0	0	3.0	2.5					
0	4	0	11.0	-12.2	2	3	3	-.7	-1.3	4	-1	4	6.7	-6.4	8	0	1	4.1	-6.2	8	0	1	4.1	-6.2	8	0	1	4.1	-6.2					
0	4	1	6.9	6.5	2	3	0	12.1	11.3	4	-2	1	10.2	-15.0	8	0	2	6.8	6.7	8	0	2	6.8	6.7	8	0	2	6.8	6.7					
0	4	2	6.5	-5.4	2	3	1	1.1	-1.1	4	-2	2	6.8	6.4	8	0	3	10.8	-8.5	8	0	3	10.8	-8.5	8	0	3	10.8	-8.5					
0	4	3	0.5	-.2	2	3	2	10.3	9.4	4	-2	3	3.0	2.7	8	1	1	6.7	5.8	8	1	1	6.7	5.8	8	1	1	6.7	5.8					
0	5	1	1.8	-1.6	2	3	3	5.6	-6.9	4	-2	4	8.1	-7.4	8	1	2	1.0	-1.0	8	1	2	1.0	-1.0	8	1	2	1.0	-1.0					
0	5	2	37.9	38.9	2	4	0	8.9	8.0	4	-3	1	7.7	-7.4	8	1	3	3.6	-3.2	8	1	3	3.6	-3.2	8	1	3	3.6	-3.2					
0	5	3	4.8	-4.4	2	4	1	10.4	10.4	4	-3	2	1.1	-1.1	8	1	4	5.5	4.6	8	1	4	5.5	4.6	8	1	4	5.5	4.6					
0	5	4	8.9	-8.4	2	4	2	9.4	-9.1	4	-3	1	1.1	-1.1	8	1	5	3.0	-2.8	8	1	5	3.0	-2.8	8	1	5	3.0	-2.8					
0	5	5	4.1	4.0	2	5	0	10.0	9.1	4	-3	4	6.7	-6.1	8	1	6	8.1	7.2	8	1	6	8.1	7.2	8	1	6	8.1	7.2					
0	5	6	5.1	-5.0	2	5	1	6.2	-5.3	4	-4	1	10.4	-9.8	8	1	7	6.6	6.2	8	1	7	6.6	6.2	8	1	7	6.6	6.2					
0	5	7	2.3	2.4	2	5	1	-.6	-1.3	4	-4	2	1.8	-1.4	8	1	8	1.1	1.4	8	1	8	1.1	1.4	8	1	8	1.1	1.4					
0	6	2	-.3	-.4	2	5	2	8.4	7.3	4	-4	3	-.5	-.4	8	1	9	1.1	1.6	8	1	9	1.1	1.6	8	1	9	1.1	1.6					
0	6	3	6.1	4.4	2	5	3	16.1	-13.6	4	-5	1	3.9	-3.8	8	1	10	7.7	-2.7	8	1	10	7.7	-2.7	8	1	10	7.7	-2.7					
0	6	4	-.6	-.6	2	5	4	9.8	9.4	4	-5	2	8.1	-7.8	8	2	1	1.1	-1.2	8	2	1	1.1	-1.2	8	2	1	1.1	-1.2					
0	6	5	2.0	-2.7	2	5	5	1.6	5.2	4	-5	0	1.6	-1.7	8	2	2	3.1	-1.2	8	2	2	3.1	-1.2	8	2	2	3.1	-1.2					
0	6	6	1.0	5.2	2	5	6	7.1	-6.1	4	-5	1	11.4	-10.7	8	2	3	1.6	1.6	8	2	3	1.6	1.6	8	2	3	1.6	1.6					
0	6	7	8.3	-8.5	2	5	7	8.2	7.6	4	-5	2	9.0	-7.9	8	2	4	1.1	1.2	8	2	4	1.1	1.2	8	2	4	1.1	1.2					
0	7	0	5.2	4.7	2	6	2	18.8	-20.7	4	-6	1	1.2	-1.4	8	3	1	1.2	-1.4	8	3	1	1.2	-1.4	8	3	1	1.2	-1.4					
0	7	1	6.5	-.6	2	6	1	3.0	-2.2	4	-6	1	1.8	-1.1	8	3	2	7.4	-12.6	8	3	2	7.4	-12.6	8	3	2	7.4	-12.6					
0	7	2	2.0	1.4	2	6	2	8.5	-7.8	4	-6	1	7.8	-8.5	8	3	3	2.1	2.0	8	3	3	2.1	2.0	8	3	3	2.1	2.0					
0	7	3	3.4	3.7	2	6	3	4.1	-3.4	4	-6	2	4.9	-4.2	8	3	4	1.0	-.8	8	3	4	1.0	-.8	8	3	4	1.0	-.8					
0	7	4	2.5	2.2	2	6	4	1.8	-1.4	4	-6	3	3.5	-3.0	8	3	5	1.2	1.2	8	3	5	1.2	1.2	8	3	5	1.2	1.2					
0	7	5	4.6	-4.2	2	6	4	8.1	7.8	4	-6	0	2.6	-2.4	8	3	6	2.6	-2.4	8	3	6	2.6	-2.4	8	3	6	2.6	-2.4					
0	7	6	7.5	7.7	2	6	5	2.9	-2.3	4	-6	1	-.4	-1.1	8	3	7	1.9	-1.9	8	3	7	1.9	-1.9	8	3	7	1.9	-1.9					
0	7	7	5.1	-5.4	2	6	6	2.2	2.2	4	-6	2	1.1	-1.1	8	3	8	1.8	-.6	8	3	8	1.8	-.6	8	3	8	1.8	-.6					
0	8	0	4.2	4.9	2	6	7	2.8	-3.2	4	-6	3	4.2	-4.3	8	3	9	1.1	1.1	8	3	9	1.1	1.1	8	3	9	1.1	1.1					
0	8	1	11.5	-13.6	2	6	8	3.5	3.1	4	-6	4	3.6	-4.3	8	3	10	1.1	1.1	8	3	10	1.1	1.1	8	3	10	1.1	1.1					
0	8	2	7.7	7.4	2	6	9	6.8	6.5	4	-6	5	1.8	-1.7	8	3	11	1.8	-1.6	8	3	11	1.8	-1.6	8	3	11	1.8	-1.6					
0	8	3	8.3	-8.5	2	6	10	8.2	7.6	4	-6	6	1.1	-1.0	8	3	12	2.6	-2.4	8	3	12	2.6	-2.4	8	3	12	2.6	-2.4					
0	8	4	6.0	-7.5	2	6	11	13.6	-11.8	4	-6	7	1.1	-1.2	8	3	13	3.6	-3.4	8	3	13	3.6	-3.4	8	3	13	3.6	-3.4					
0	8	5	6.7	7.2	2	6	12	7.5	7.1	4	-6	8	1.4	-.6	8	3	14	4.2	-4.0	8	3	14	4.2	-4.0	8	3	14	4.2	-4.0					
0	8	6	3.0	10.8	-12.4	2	6	13.6	-12.2	4	-6	9	1.4	-.6	8	3	15	5.1	-4.9	8	3	15	5.1	-4.9	8	3	15	5.1	-4.9					
0	8	7	23.4	26.9	2	6	14	26.8	26.5	4	-6	10	11.2	-10.5	8	3	16	6.1	-5.9	8	3	16	6.1	-5.9	8	3	16	6.1	-5.9					
0	9	0	2.5	3.8	2	6	15	3.1	-2.2	4	-6	11	2.2	-1.9	8	3	17	6.4	-6.2	8	3	17	6.4	-6.2	8	3	17	6.4	-6.2					
0	9	1	11.2	-10.1	2	6	16	11.1	-10.1	4	-6	12	1.3	-1.2	8	3	18	7.1	-6.9	8	3	18	7.1	-6.9	8	3	18	7.1	-6.9					
0	9	2	6.1	5.6	2	6	17	7.9	-7.9	4	-6	13	1.1	-1.1	8	3	19	7.8	-7.6	8	3	19	7.8	-7.6	8	3	19	7.8	-7.6					
0	9	3	53.9	50.0	2	6	18	5.9	4.8	4	-6	14	1.1	-1.1	8	3	20	8.5	-8.3	8	3	20	8.5	-8.3	8	3	20	8.5	-8.3					
0	9	4	1.7	-1.5	2	6	19	2.2	-2.2	4	-6	15	1.1	-1.1	8	3	21	9.2	-9.0	8	3	21	9.2	-9.0	8	3	21	9.2	-9.0					
0	9	5	8.8	-8.4	2	6	20	11.1	-11.1	4	-6	16	1.1	-1.1	8	3	22	10.0	-9.8	8	3	22	10.0	-9.8	8	3	22	10.0	-9.8					
0	9	6	9.1	8.7	2	6	21	8.6	-8.5	4	-6	17																						

Table 7. Least-squares planes.

The equation of the plane is  $Ax + By' + Cz^* = D$  where  $x$ ,  $y'$ , and  $z^*$  are respectively orthogonalized axes, and  $D$  is set equal to the perpendicular distance from the origin to the plane.

Plane	A	B	C	D
(110)	0.5343	0.7198	0.4432	5.3901 Å
$m^a$	0.5052	0.8291	0.2397	4.9739
(45Å) <sup>b</sup>	0.4835	0.8436	0.2335	4.8780

<sup>a</sup>Deviations of the interatomic midpoints from this plane:

C(1)-C(2) 0.0012 Å  
 C(3)-C(10) -0.0014  
 C(4)-C(5) -0.0005  
 C(6)-C(7) 0.0013  
 C(8)-C(9) -0.0005

<sup>b</sup>This plane is determined by the points (1,0,0), (0,.8,0), and (-4,0,0) and contains the point (½,½,½).

Table 8. Statistical comparisons of bond lengths and angles.

The largest difference in C-C-C bond angles related by the mirror plane of dibasketene is  $1.5^\circ$ . The esd of this difference is  $0.85^\circ$ . The probability of observing so large a relative difference is 0.08. Since there are 15 such pairs of mirrored angles, this difference is not significant. Similarly:

Compared quantities	Largest difference	Esd of difference	Probability	No. of pairs
mirrored C-C-H angles	$13^\circ$	$7.4^\circ$	0.08	15
mirrored C-C lengths	$0.01\text{\AA}$	$0.014\text{\AA}$	0.48	5
mirrored C-H lengths	$0.11\text{\AA}$	$0.12\text{\AA}$	0.36	5
C-C lengths in $\underline{2}$ and $\underline{4}$	$0.04\text{\AA}$	$0.022\text{\AA}$	0.07	15
C-C-C angles in $\underline{2}$ and $\underline{4}$	$1.4^\circ$	$1.12^\circ$	0.42	26

"Chemistry remains an experimental science."

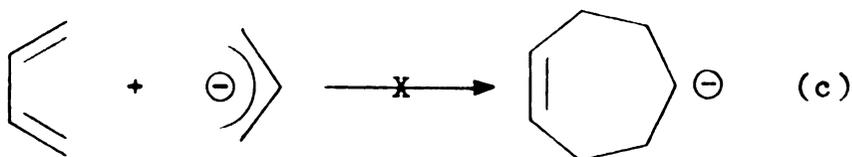
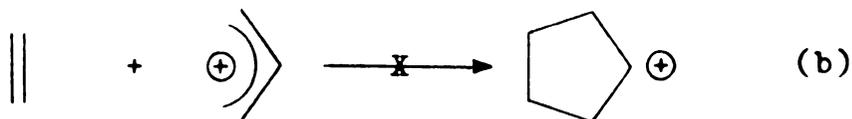
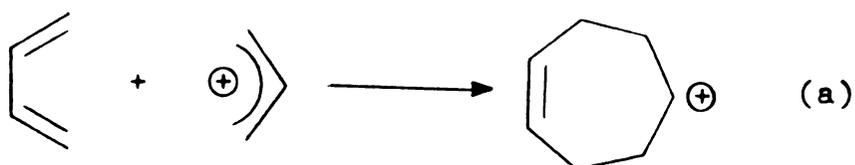
R.B. Woodward

PART II

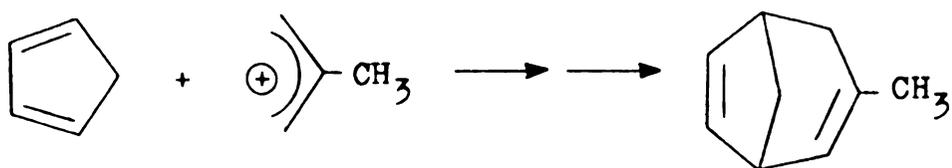
The Reaction of Allyl Lithium with Stilbene

## INTRODUCTION

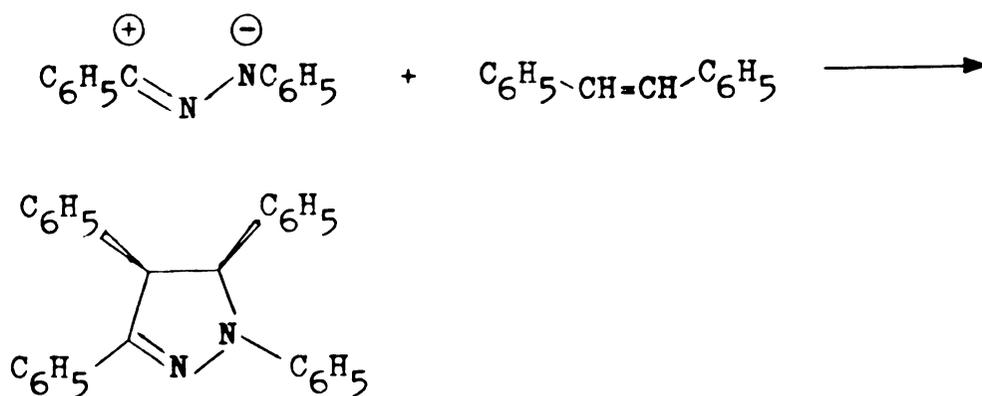
The Woodward-Hoffmann orbital symmetry rules (17) predict that the following thermal  $[n + 3]$  cycloaddition reactions will occur, or not occur, concertedly:



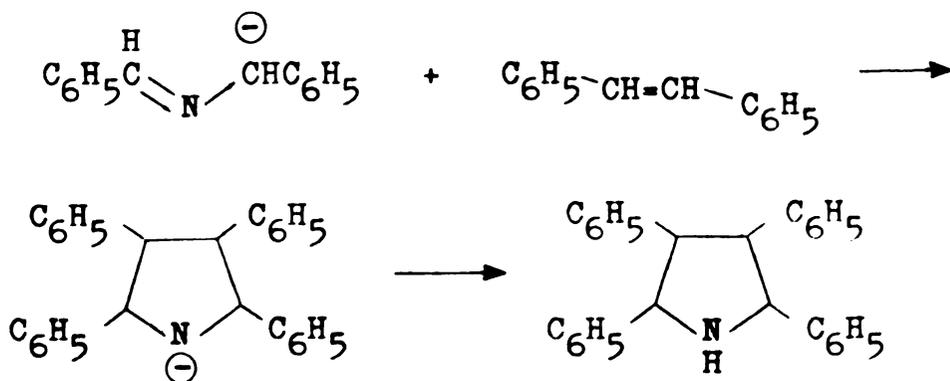
A reaction of the type (a) has been carried out (18); but its concertedness has not been demonstrated.



Many cases of concerted heterocycloadditions of the type (d) are known. The largest class of these consists of the 1,3-dipolar additions, for example

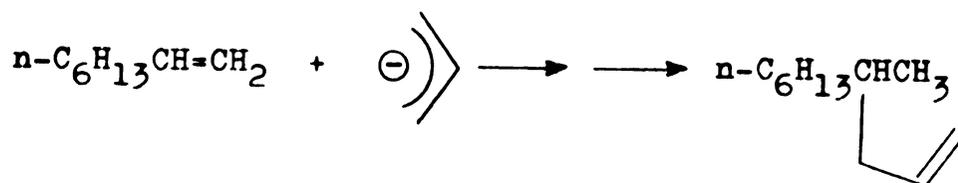


which have been extensively studied and reviewed (19) by Huisgen. An anionic cycloaddition of the type (d) has also been carried out (20); but, again, its concertedness has not been demonstrated.



This reaction probably succeeds, whether it is concerted or not, because the negative charge in the product is localized on a more electronegative atom than carbon; and it is probably because of the thermodynamically unfavorable charge localization that no pure carbocycloadditions of the type (d) are known (21).

Allyl anions have been observed to react with certain terminal olefins, but only by 1,2 addition (22)

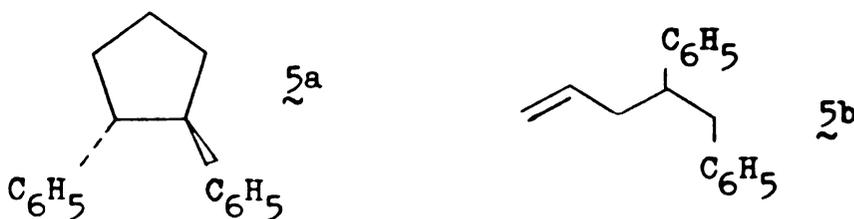


and to initiate the polymerization of styrene (23).

However, it was hoped that a nonterminal, polymerization-resistant olefin could be found whose reaction with an allyl anion would, under the right experimental conditions, be of the type (d).

## RESULTS AND DISCUSSION

Accordingly, the following reaction was tried: An ethereal solution of allyl lithium was refluxed with an equimolar amount of trans-stilbene for an hour. The usual workup procedures produced a yellow oil, containing no stilbene, which solidified after standing for several days. Recrystallization of the crude solid gave a white powder, 5, with a melting point of 145-47°. The two expected products, 5a and 5b, melt at 66° (24) and <25° (25) respectively.

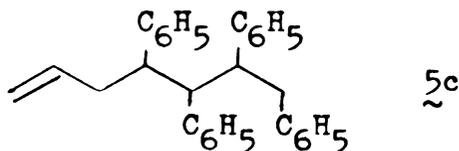


The characterization of the actual product required a thorough spectroscopic investigation.

Elemental analysis and mass spectrometry established the empirical formula of 5 as  $C_{31}H_{30}$ --a molecule constructed from two stilbene molecules, an allyl group, and a hydrogen atom.

The infrared spectrum of 5, Figure 4, shows both

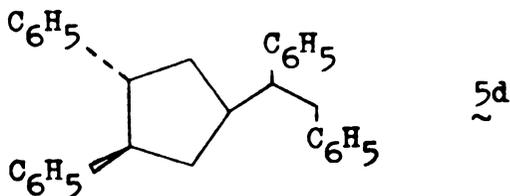
saturated aliphatic and aromatic C-H stretching bands and a typical monoalkyl substituted phenyl absorption pattern; but it does not show, as does  $\underline{5b}$ , a vinyl group band at  $1640\text{ cm}^{-1}$ .  $\underline{5c}$  was therefore immediately excluded as a possible structure.



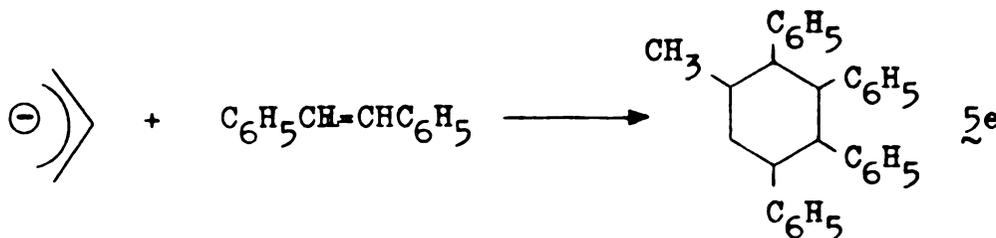
The ultraviolet spectrum of  $\underline{5}$ , Figure 5, has  $\lambda_{\text{max}} = 260\text{ nm}$  with fine structure and  $\epsilon = 891\text{ l/cm-mole}$ . The four phenyl rings in  $\underline{5}$  are therefore unconjugated, and the remaining double bond equivalent required by the empirical formula may well be a ring.

The 60 mc NMR spectrum of  $\underline{5}$ , Figure 6a, shows the 20 aryl hydrogens as a pair of pseudo singlets at  $\delta 7.00$  and  $\delta 6.76$  and the 10 aliphatic hydrogens as a complex multiplet between  $\delta 3.8$  and  $\delta 1.0$ .

On the basis of this information, structure  $\underline{5d}$ , which could have arisen from a  $[2 + 3]$  cycloaddition followed by a simple 1,2 addition to stilbene, was postulated.



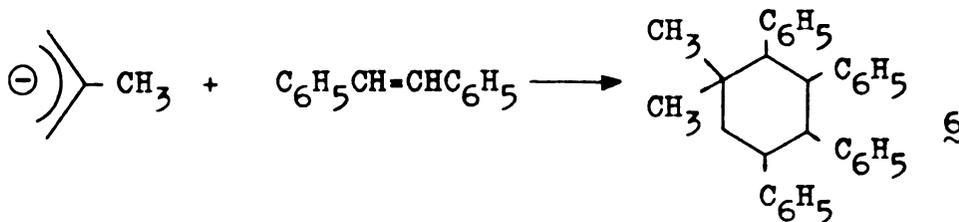
However, structure  $\underline{5}e$  is also consistent with the above spectral data; and it alone can explain the 100 mc NMR spectrum of  $\underline{5}$ , Figure 6b.



At 100 mc the 4 benzylic hydrogens in  $\underline{5}e$  appear as a multiplet at  $\delta 3.79-2.76$ , the 3 homobenzylic hydrogens as a multiplet at  $\delta 2.51-1.86$ , and the methyl group as a doublet,  $J = 7.0$  cps, at  $\delta 1.09$ . Furthermore, irradiation of the spectrum at  $\delta 2.33$  causes the methyl group doublet to collapse to a broad singlet (see Figure 7).

Nothing can be said about the stereochemistry of  $\underline{5}$ . Its methyl resonance does resemble that of cis-1-methyl-4-phenylcyclohexane, in which the methyl group is confined almost exclusively to an axial position, and is quite unlike that of the corresponding trans isomer in which the methyl group is necessarily equatorial (26) (see Figure 8); but the structures are too dissimilar to allow any reliable stereochemical inferences.

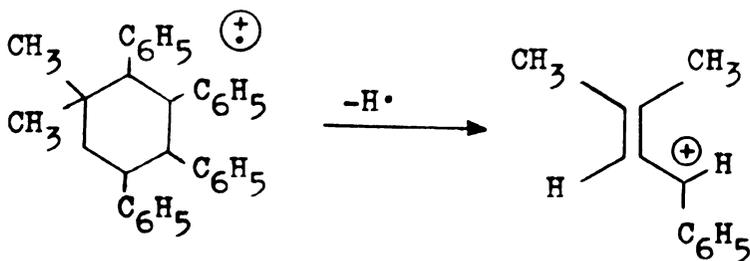
$\underline{5}$  could not be dehydrogenated, by any of a variety of methods, to 1-methyl-2,3,4,5-tetraphenylbenzene. Confirmation of the structural assignment  $\underline{5}e$  was therefore sought and found in the comparative spectral properties of  $\underline{6}$ , obtained by reacting  $\beta$ -methallyl lithium with stilbene.



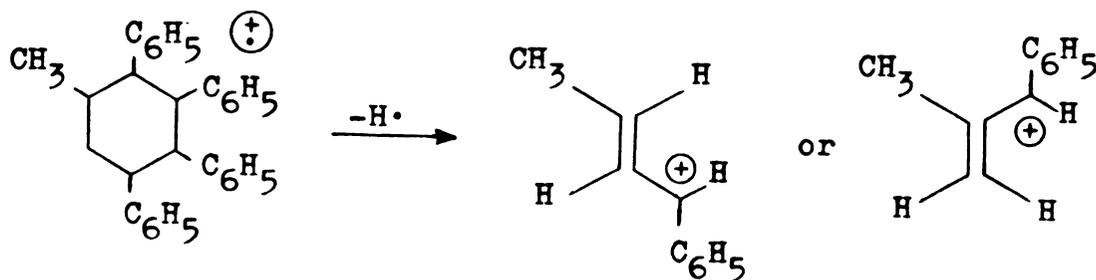
Elemental analysis and mass spectrometry established the empirical formula of  $\underline{6}$  as  $\text{C}_{32}\text{H}_{32}$ .

The infrared spectrum of  $\underline{6}$ , Figure 9, closely resembles that of  $\underline{5}$  but has a strong doublet between 1350 and 1400  $\text{cm}^{-1}$  characteristic of the gem-dimethyl group. The strong band in the infrared spectrum of  $\underline{5}$  at 1375  $\text{cm}^{-1}$  can therefore be assigned to the scissoring vibration of the methyl hydrogens.

The mass spectral fragmentation pattern of  $\underline{6}$  aids in the understanding of that of  $\underline{5}$ . Peaks at  $m/e = 180$  (stilbene) and  $m/e = 91$  (tropylium ion) are prominent in both spectra, Figures 10 and 11; but the base peak in the spectrum of  $\underline{6}$  occurs at  $m/e = 145$  and undoubtedly arises in the following way:

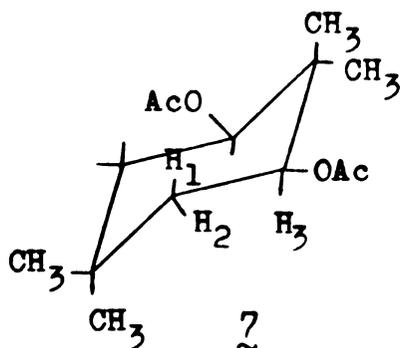


By analogy, the moderately abundant fragment in the spectrum of 5 at  $m/e = 131$  can be accounted for in two ways.



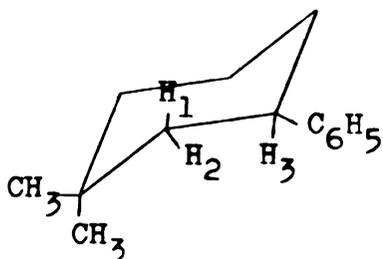
The 60 mc NMR spectrum of 6, Figure 12, shows the 20 aryl hydrogens as a pair of pseudo singlets at  $\delta 7.01$  and  $\delta 6.80$ , the four benzylic hydrogens as a multiplet at  $\delta 3.8-2.7$ , the two homobenzylic hydrogens as a multiplet at  $\delta 2.4-1.7$ , and the methyl groups as a pair of singlets at  $\delta 1.25$  and  $\delta 0.88$ .

The benzylic and homobenzylic hydrogens of 6 constitute a six-spin ABCDMN system. An analysis of the MN portion of the spectrum was carried out using the LAOCN3 computer program (27). Initial input data were taken from compound 7 (28);



$$\begin{aligned}
 \nu_1 - \nu_2 &= 7.9 \text{ cps} \\
 J_{1,2} &= -12.4 \text{ cps} \\
 J_{1,3} &= 12.4 \text{ cps} \\
 J_{2,3} &= 4.3 \text{ cps}
 \end{aligned}$$

and it was assumed that all the phenyl rings occupy equatorial positions, hence the  $J_{vic}$ 's = 12.4 cps and that  $\nu_4 = \nu_5 = \delta 3.1$  and  $\nu_3 = \nu_6 = \delta 3.4$ . The chemical shifts and coupling constants which best fit the observed spectrum of **6** are listed below; and the calculated and observed spectra are shown in Figure 13.



$$\begin{aligned} \nu_1 &= 116.1 (\pm 0.3) \text{ cps from TMS} \\ \nu_2 &= 110.7 (\pm 0.3) \text{ cps from TMS} \\ J_{1,2} &= -14.0 (\pm 0.1) \text{ cps} \\ J_{1,3} &= 12.6 (\pm 0.6) \text{ cps} \\ J_{2,3} &= 3.2 (\pm 0.6) \text{ cps} \end{aligned}$$

The structural similarity of **6** and **7** is confirmed by these data.

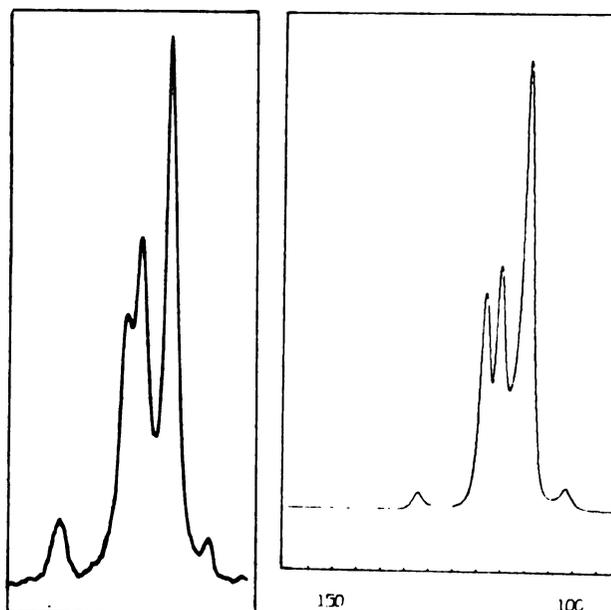
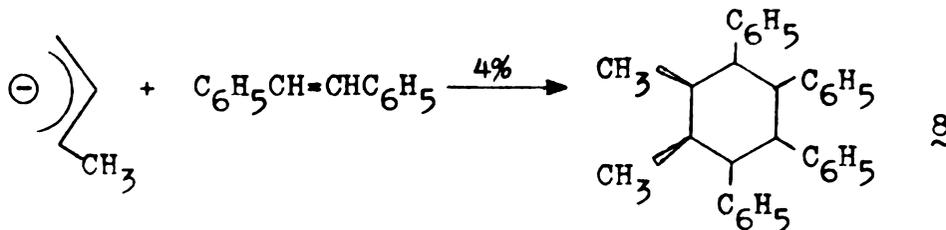


Figure 13. The calculated and observed NMR spectra of compound **6**.

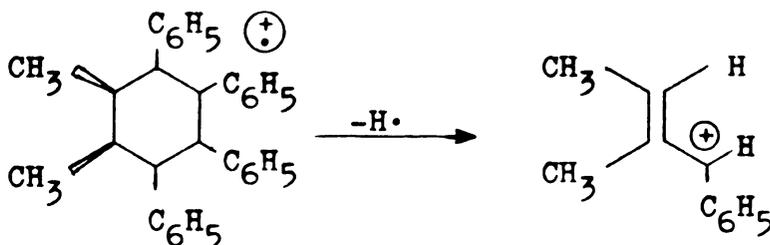
To explore this reaction further,  $\alpha$ -methallyl lithium was reacted with stilbene, and the only product that could be isolated was **8**.



Elemental analysis and mass spectrometry established the empirical formula of **8** as  $\text{C}_{32}\text{H}_{32}$ .

The infrared spectrum of **8**, Figure 14, very closely resembles that of **5**, but the band at  $1375\text{ cm}^{-1}$ , the scissoring vibration of the methyl hydrogens, is relatively more intense.

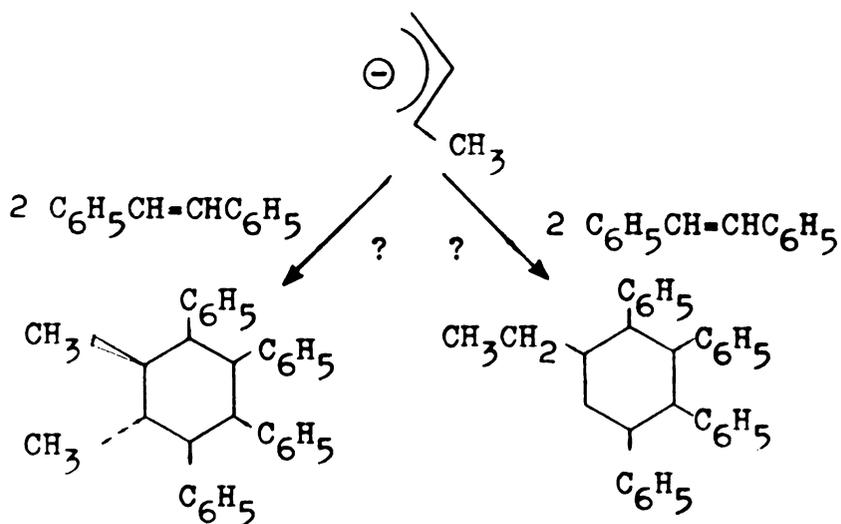
The mass spectrum of **8**, Figure 15, is also quite similar to that of **5**, but, as in the case of **6**, the base peak occurs at  $m/e = 145$ .



The 60 mc NMR spectrum of **8**, Figure 16, shows the 20 aryl hydrogens as a multiplet at  $\delta 7.1$  and a pseudo singlet at  $\delta 6.87$ , the 4 benzylic and 2 homobenzylic hydrogens as a very complex multiplet between  $\delta 4.0$  and

$\delta$ 1.9, and the methyl groups as a pair of doublets at  $\delta$ 1.00,  $J = 7.6$  cps, and  $\delta$ 0.73,  $J = 6.2$  cps. If an all equatorial, all 1,2 trans, arrangement of the phenyl rings can be assumed, the methyl groups must be cis by virtue of their magnetic nonequivalence.

While there is precedent for the reaction of the  $\alpha$ -methallyl carbanion with olefins at C-1 rather than at C-3 (22), it must be emphasized that **8** is merely the only product that has been isolated from the reaction mixture. Other isomers of **8** may account for the remaining 96% of the yield.



A proposed mechanism for the reaction of allyl lithium with stilbene is presented in Figure 17. Several experimental observations are relevant to this mechanism.

(a) Both cis and trans stilbene react with allyl lithium to give only  $\underline{5}$ . This requires intermediates like the 4,5-diphenyl-1-pentene-5-yl anion in which free rotation about the bond between the benzylic carbons is possible.

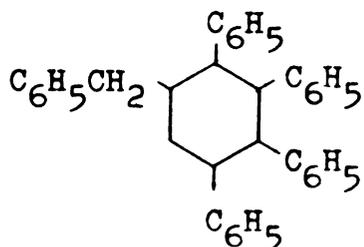
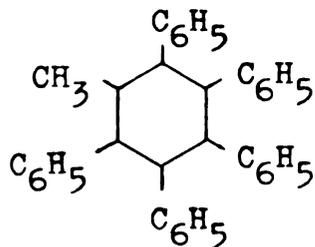
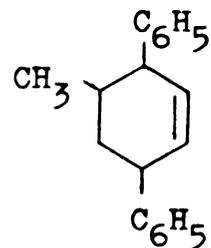
(b) When the reaction is worked up with  $D_2O$  instead of  $H_2O$  no deuterium is incorporated into  $\underline{5}$ . The solvent is the most likely internal proton source.

(c) Although the reaction produces  $\underline{5}$  in a nearly quantitative yield, a small amount of trans-1,2-diphenylcyclopentane is in fact formed and can be detected and identified by gas-liquid chromatography (see Figure 18).

(d) The cleavage of allyl phenyl ether with lithium gives allyl lithium in only about 60% yield (29); but no unreacted ether contaminates the crude product  $\underline{5}$ . Lithium phenoxide is a byproduct in the cleavage reaction. Furthermore, when the blood-red solution of allyl lithium is added to the stilbene the mixture turns black; but the black color is completely discharged on quenching with water. The influence, if any, of the source of the allyl lithium on the course of the reaction could be ascertained by preparing the allyl lithium solution by cleavage of allyltriphenyltin with phenyllithium (30).

(e) When attempts were made to extend the scope of this reaction still further by preparing  $\underline{9}$  or  $\underline{10}$  by reaction

of cinnamyl lithium with stilbene and by preparing 11 by reaction of allyl lithium with diphenylbutadiene, only intractable gums resulted.

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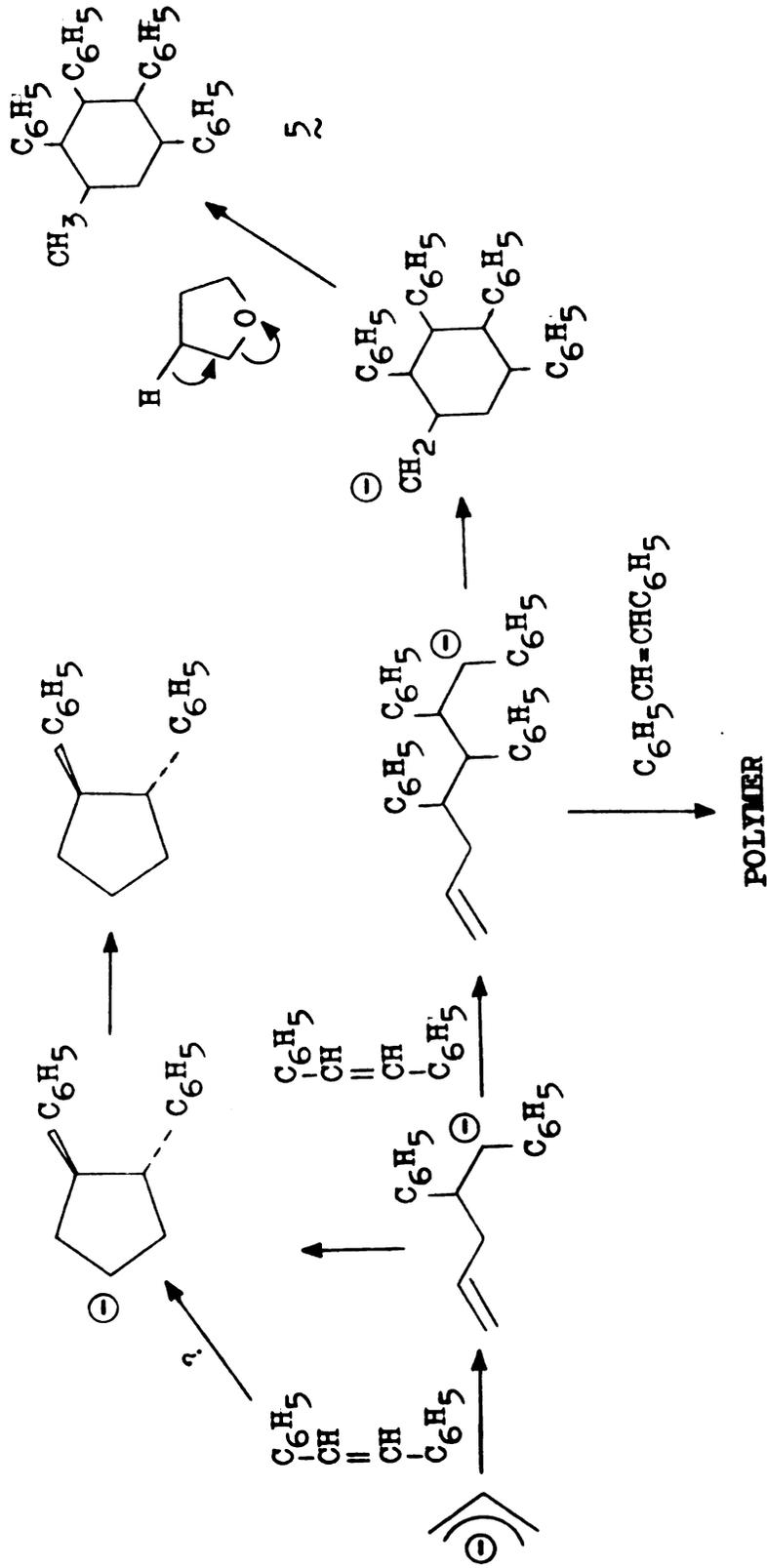
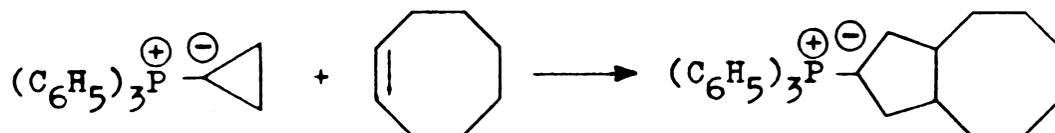


Figure 17. A proposed mechanism for the formation of compound 5.

Another approach to the  $[2+3]$  anionic carbocyclo-  
addition reaction was also tried:



This reaction has greater potential synthetic usefulness than a reaction between an allyl anion and an olefin; but it failed to occur.

## EXPERIMENTAL

### General Procedures

Infrared spectra were recorded on a Perkin-Elmer Model 137 spectrophotometer using KBr discs. NMR spectra were taken on a Varian T-60, A-56-60, or HA-100 spectrometer with samples in  $\text{CDCl}_3$  solution. Chemical shifts are reported in ppm from tetramethylsilane. Ultraviolet spectra were recorded on a Unicam Model SP-800 spectrophotometer using 1 cm quartz cells. Mass spectra were obtained with a Hitachi Perkin-Elmer RMU-6 mass spectrometer.

Gas chromatographic analyses were done on a Varian Aerograph 1200 instrument.

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Computer calculations of NMR spectra were done on a CDC-3600 computer.

Microanalyses were performed by the Spang Microanalytical Laboratory, Ann Arbor, Michigan.

1-methyl-2,3,4,5-tetraphenylcyclohexane (5).

A solution of allyl lithium in 75 ml of 2:1 (v/v) tetrahydrofuran-ether, prepared in ca. 60% yield by cleavage of 0.05 mole of allyl phenyl ether with a 12-fold excess of cut lithium wire (29), was poured through a porcelain Büchner funnel-sans-filter paper into a 200 ml 2-neck flask containing 9.0 gm (0.05 mole) of trans-stilbene (Note 1) and equipped with a reflux condenser and a nitrogen inlet and outlet system. The mixture was refluxed under nitrogen for an hour and then poured onto ice; and the product was taken up in methylene chloride, dried, and thoroughly freed of solvent under vacuum. The resulting yellow oil was dissolved in a boiling mixture of 50 ml of 95% ethanol and 10 ml of carbon tetrachloride from which the product crystallized after standing for 12 hr under refrigeration. A second recrystallization from 25 ml of heptane afforded 3.9 gm (39% yield based on stilbene) (Note 2) of a white powder, mp 145-47°.

Anal. calcd for  $C_{31}H_{30}$ : C, 92.49; H, 7.51. Found: C, 92.39; H, 7.66.

Note 1: Cis-stilbene may be used in place of trans-stilbene in the above procedure; but the allyl lithium solution must then be added slowly because of the greater initial vigor of the reaction.

Note 2: The IR and NMR spectra of the crude oil and the purified solid are nearly identical. The actual

yield of 5 is therefore almost quantitative. The crude oil was separated into its components by gas-liquid chromatography (5% SE-30/Chromosorb-W column at 210-250°). The resulting chromatogram is shown in Figure 18. The peak corresponding to trans-1,2-diphenylcyclopentane was determined by addition of an authentic sample to the oil.

Reaction of allyl lithium with stilbene under very mild conditions.

The above procedure was modified in the following way: The solution of allyl lithium was added dropwise over a period of 20 min to only 4.5 gm (0.025 mole) of trans-stilbene dissolved in 50 ml of tetrahydrofuran which was kept at 0° by means of an ice-salt bath. The mixture was stirred for an additional 10 min and was then worked up to the crude oil stage. Gas chromatographic analysis of the oil showed that the reaction had gone to completion.

trans-1,2-diphenylcyclopentane.

This compound was prepared by Clemmensen reduction of trans-3,4-diphenylcyclopentanone (31) according to Wiedlich's procedure (24). The product had the correct melting point, 66°; and its infrared spectrum showed complete reduction of the carbonyl group.

Attempted dehydrogenation of compound 5.

Compound 5 was recovered unchanged after attempted dehydrogenation with palladium on charcoal in refluxing cymene (32) and with sulfur at 220° (33) and was destroyed by attempted dehydrogenation with selenium at 320° (33).

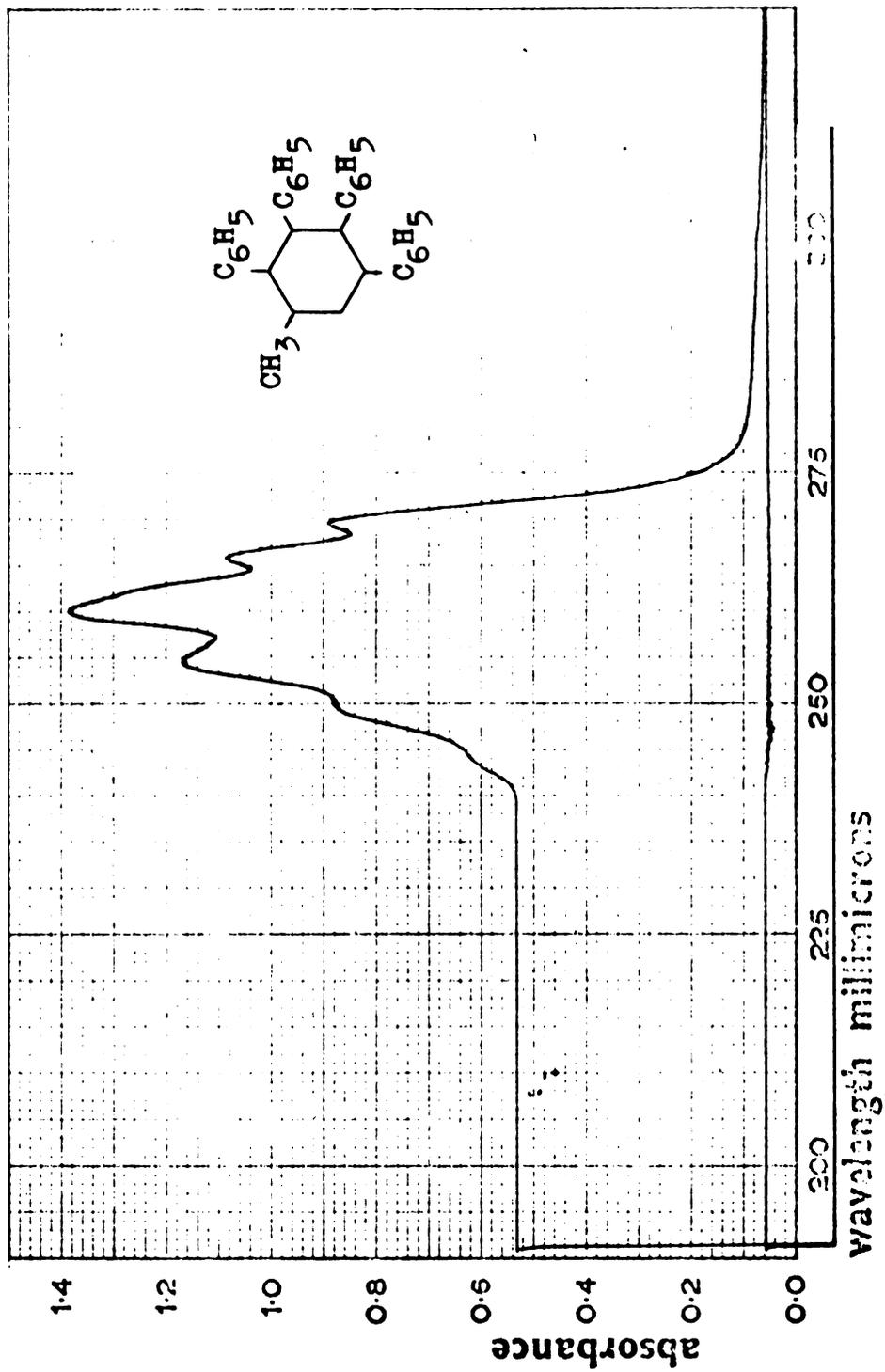


Figure 5. The ultraviolet spectrum of compound 5.  
(0.00149 M in dioxane vs. dioxane)

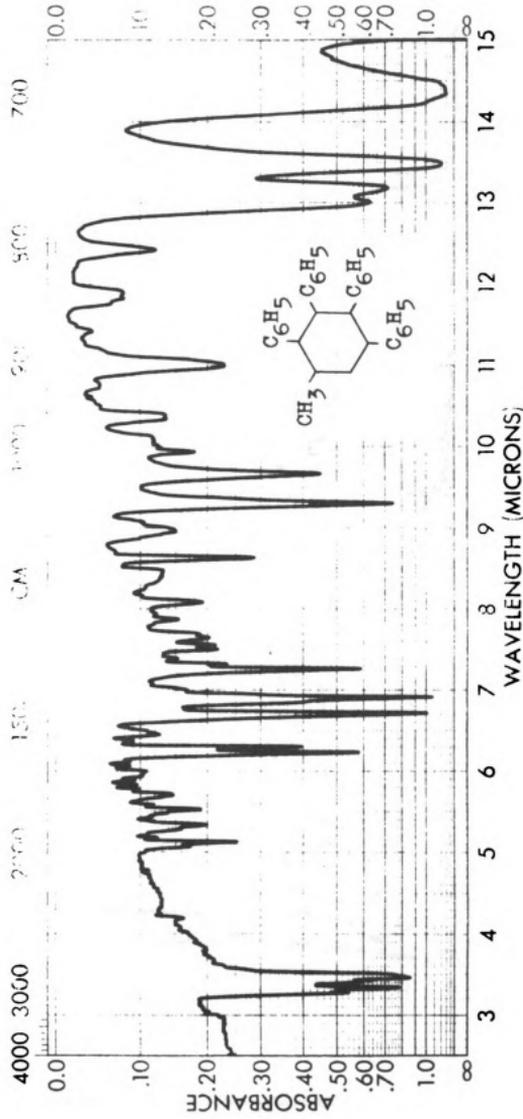
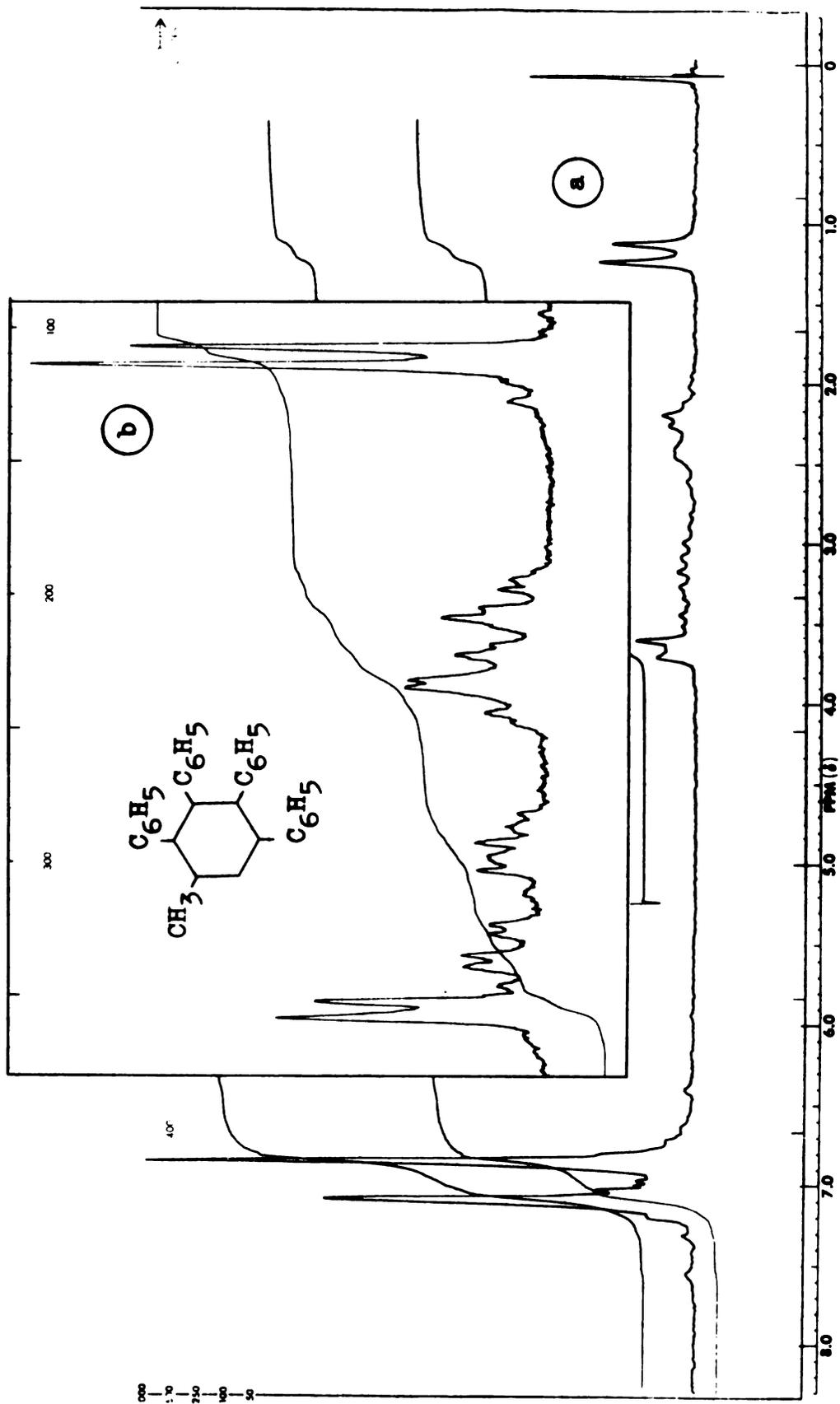


Figure 4. The infrared spectrum of compound 5.



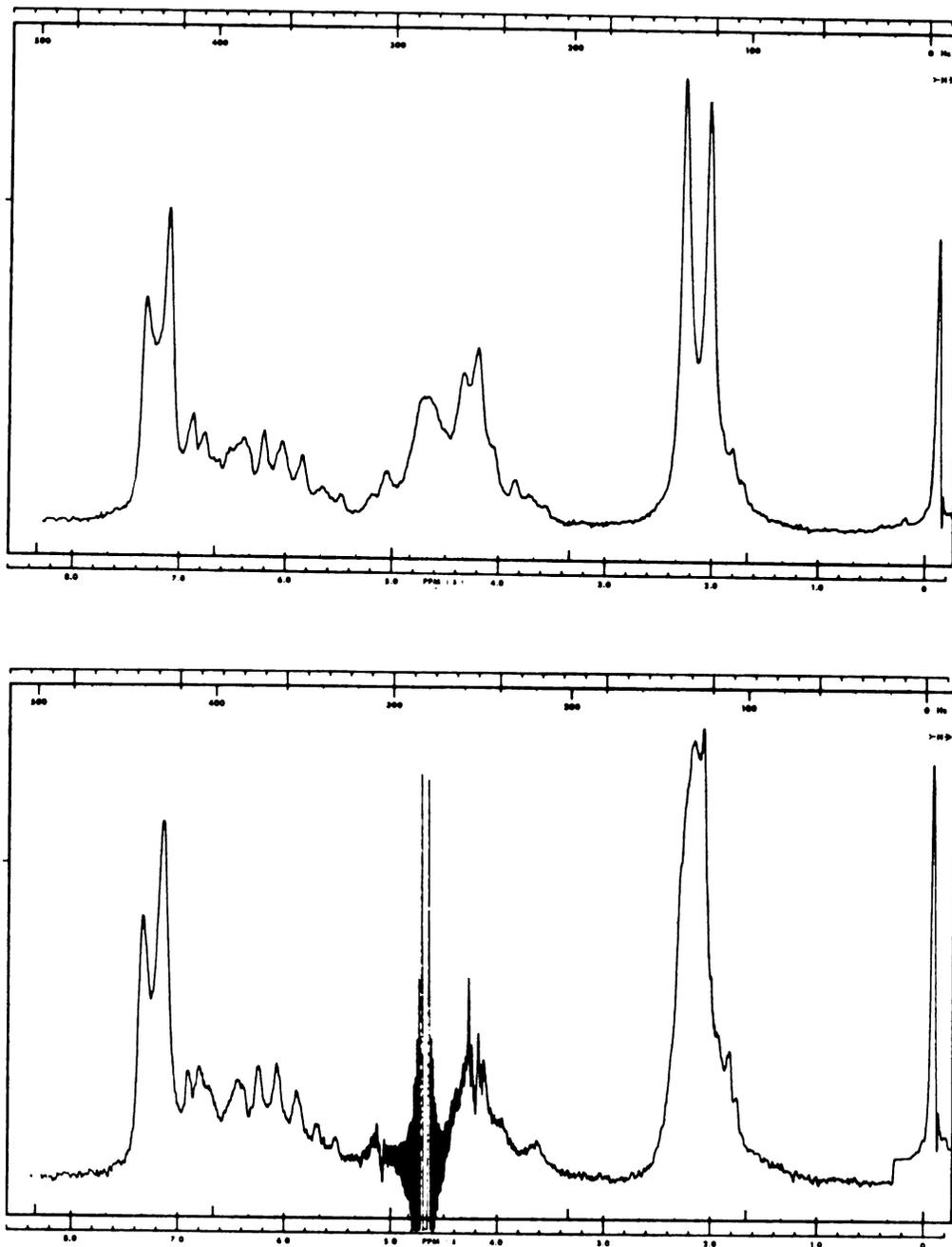


Figure 7. Irradiated frequency-sweep NMR spectrum of compound **5**.

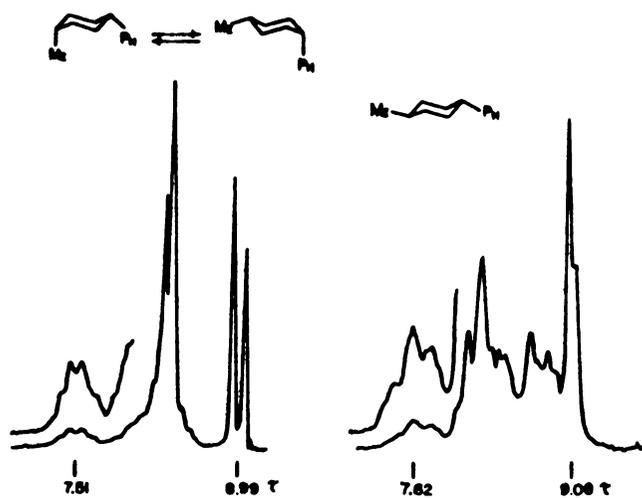


Figure 8. The NMR spectra of cis and trans 1-methyl-4-phenylcyclohexane.

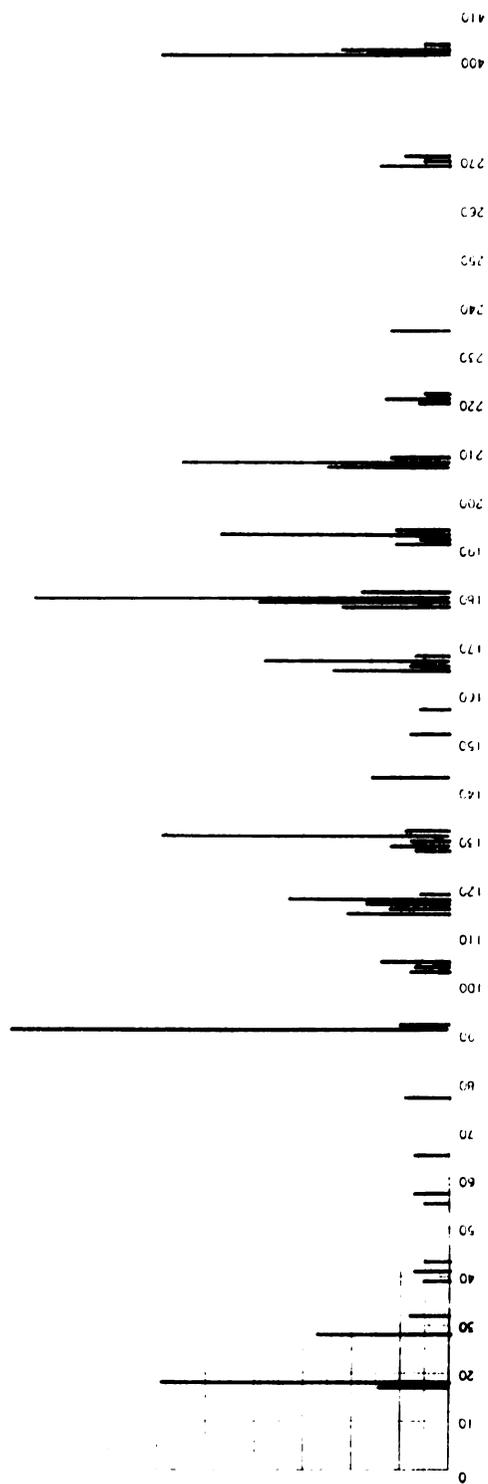
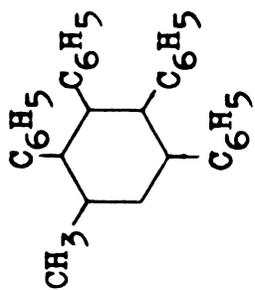


Figure 10. The mass spectrum of compound 5.

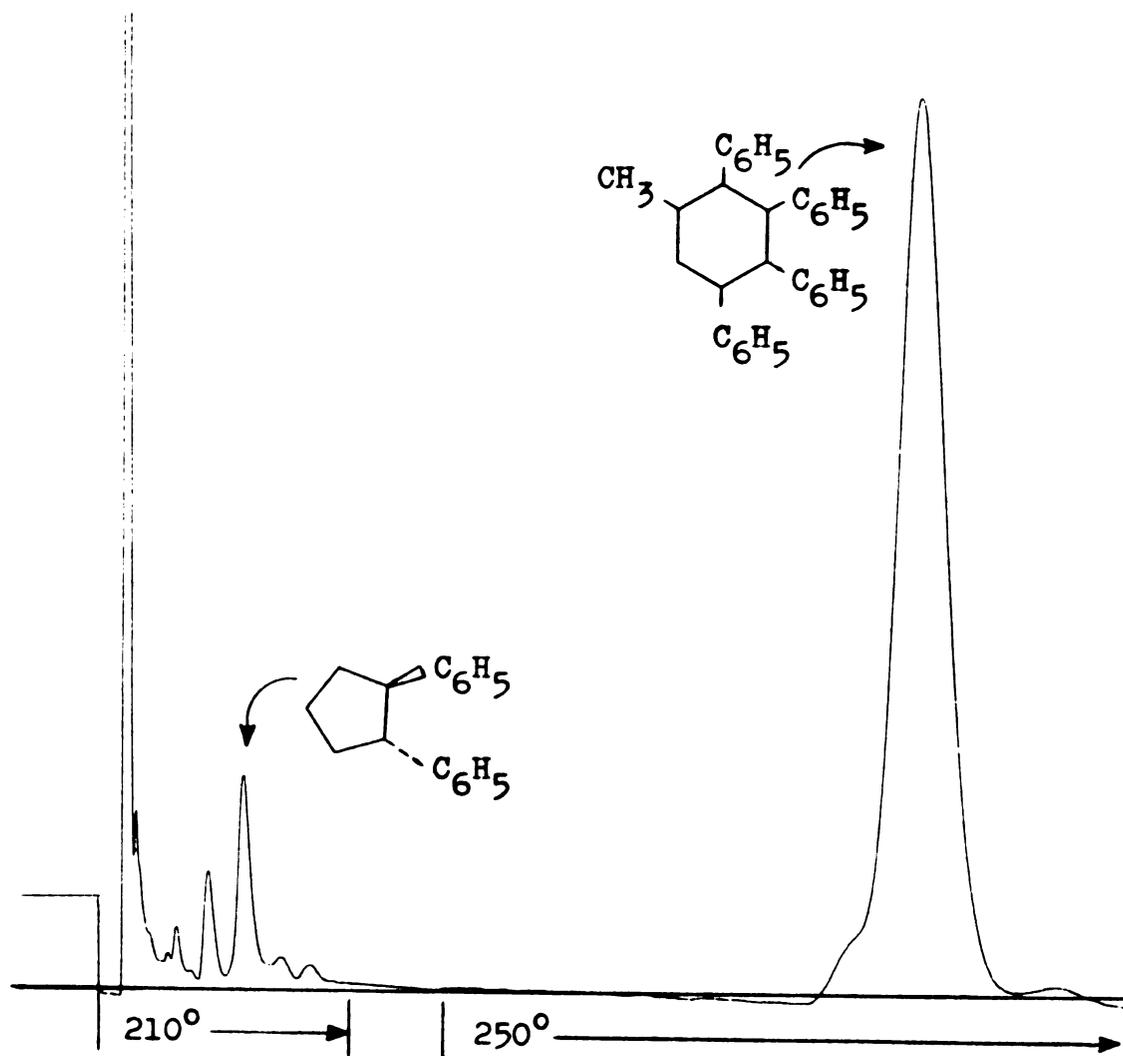


Figure 18. The gas chromatogram of crude compound 5.

1,1-dimethyl-2,3,4,5-tetraphenylcyclohexane (6).

A solution of  $\beta$ -methallyl lithium, prepared by cleavage of  $\beta$ -methallyl phenyl ether (34) with lithium, was reacted, as in the preparation of 5, with 9.0 gm (0.05 mole) of trans-stilbene. The crude oil was recrystallized from ethanol-carbon tetrachloride only to give 4.8 gm (46% yield based on stilbene) of a white powder, mp 153-55°.

Anal. calcd for  $C_{32}H_{32}$ : C, 92.26; H, 7.74. Found: C, 92.15; H, 7.80.

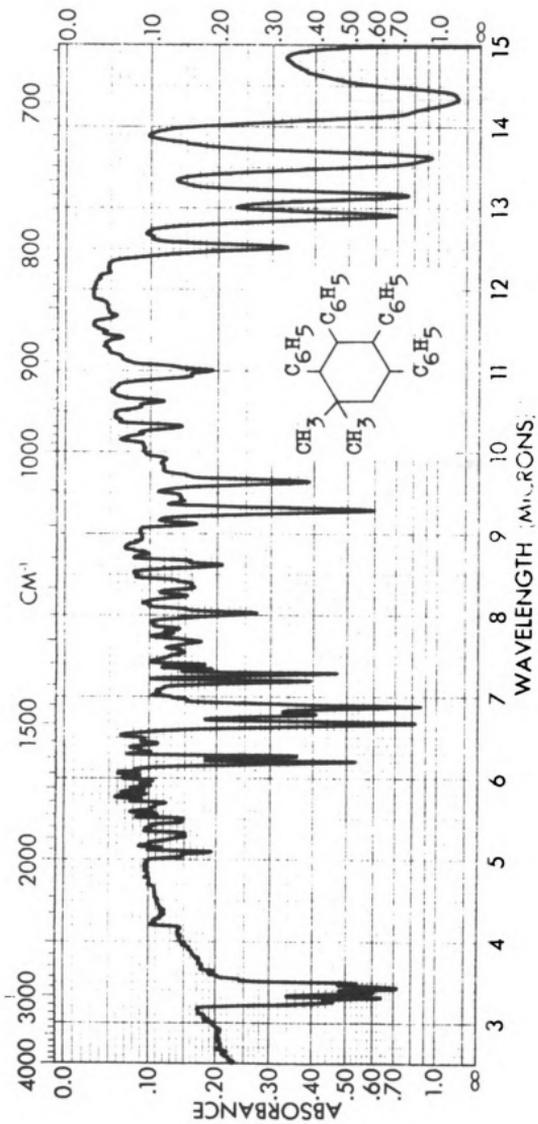


Figure 9. The infrared spectrum of compound 6.

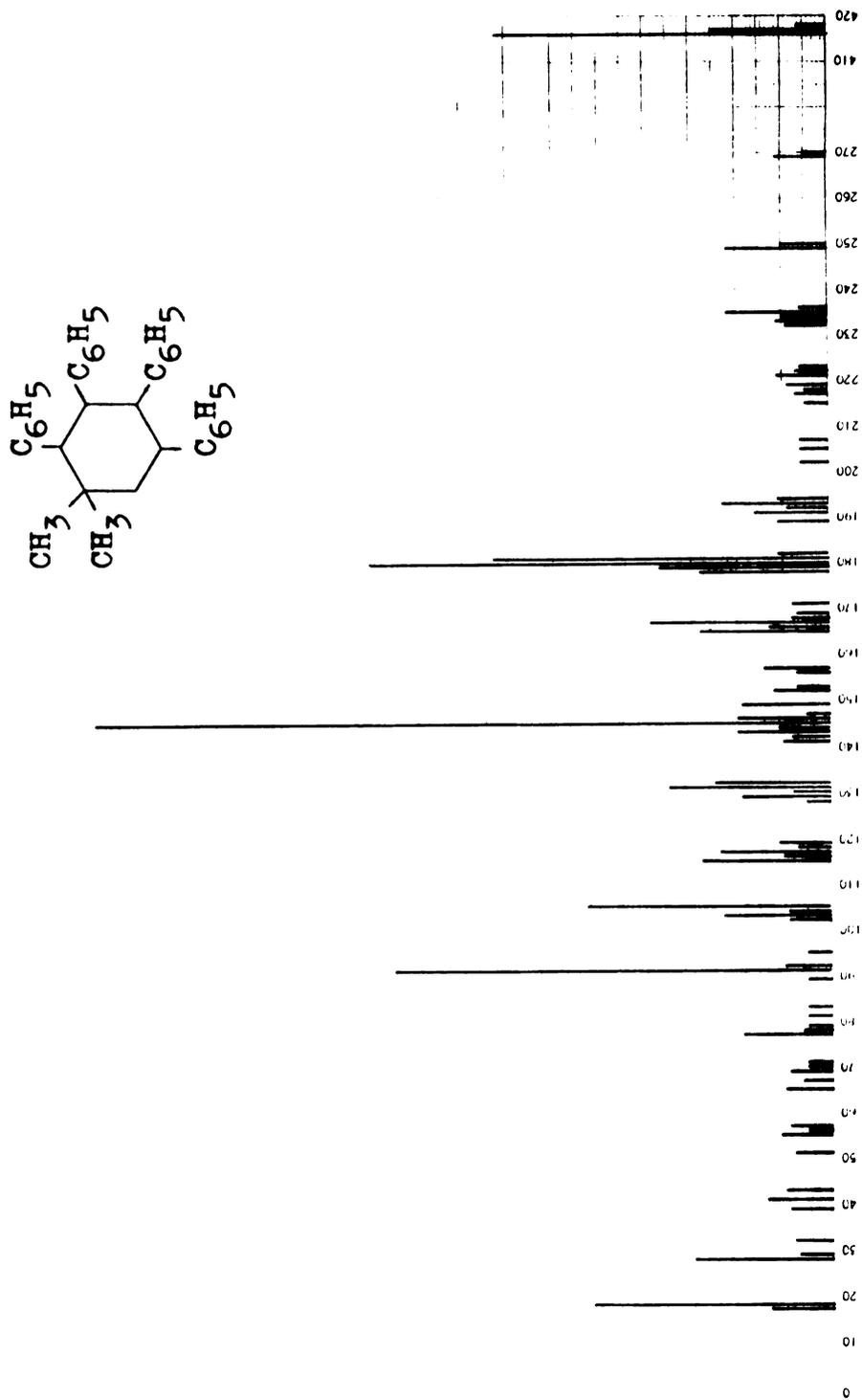


Figure 11. The mass spectrum of compound 6.

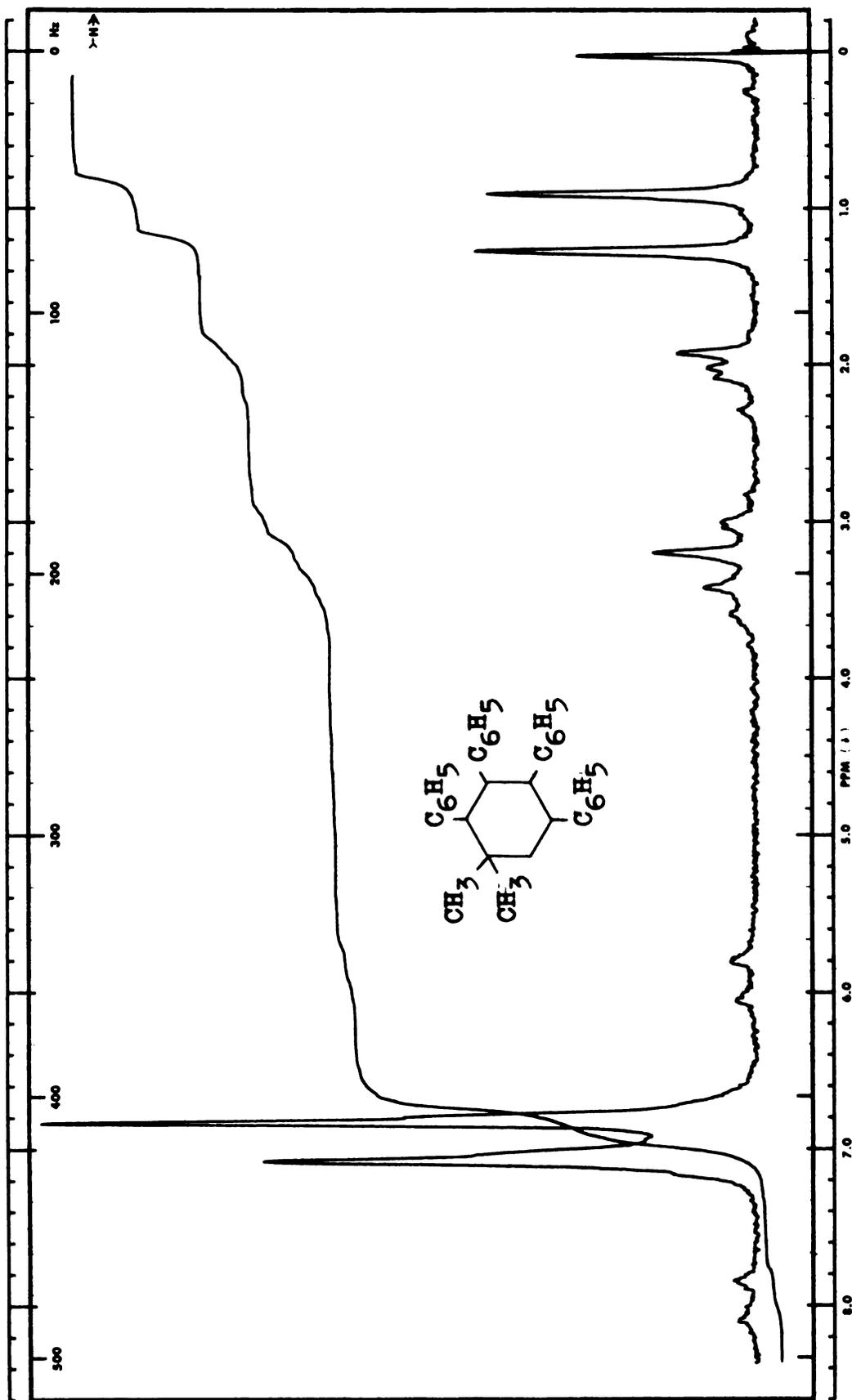


Figure 12. The 60 mc NMR spectrum of compound 6.

cis-1,2-dimethyl-3,4,5,6-tetraphenylcyclohexane (8).

A solution of  $\alpha$ -methallyl lithium, prepared by cleavage of  $\alpha$ -methallyl phenyl ether (35) with lithium, was reacted, as in the preparation of 5, with 9.0 gm (0.05 mole) of trans-stilbene. The crude oil was triturated with 20 ml of pentane; and the solid which separated was filtered off, washed with pentane, and recrystallized from 5 ml of heptane to give 370 mg (3.5% yield based on stilbene) of a white powder, mp 178-80°.

Anal. calcd for  $C_{32}H_{32}$ : C, 92.26; H, 7.74. Found: C, 92.07; H, 7.76.

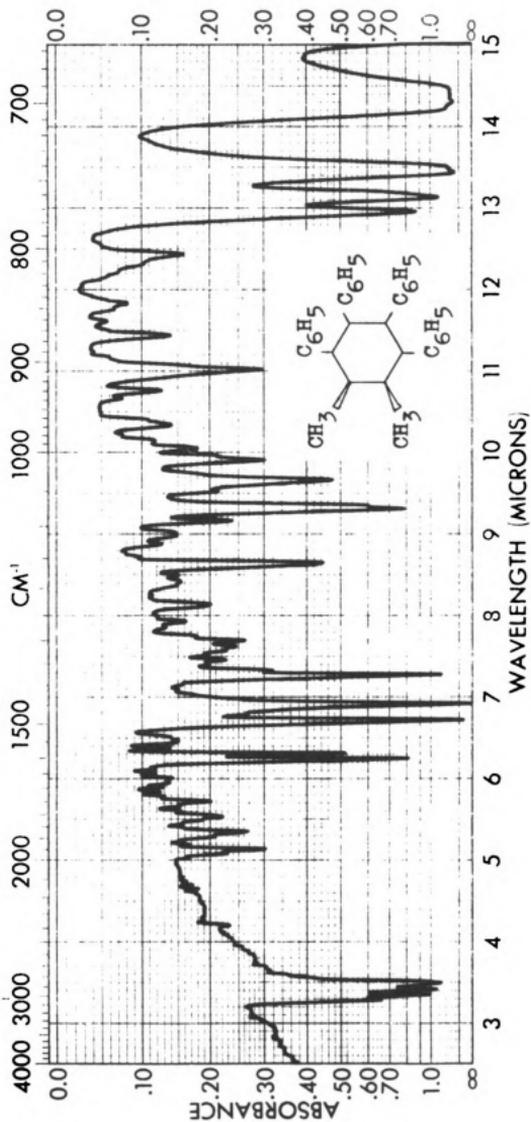


Figure 14. The infrared spectrum of compound 8.

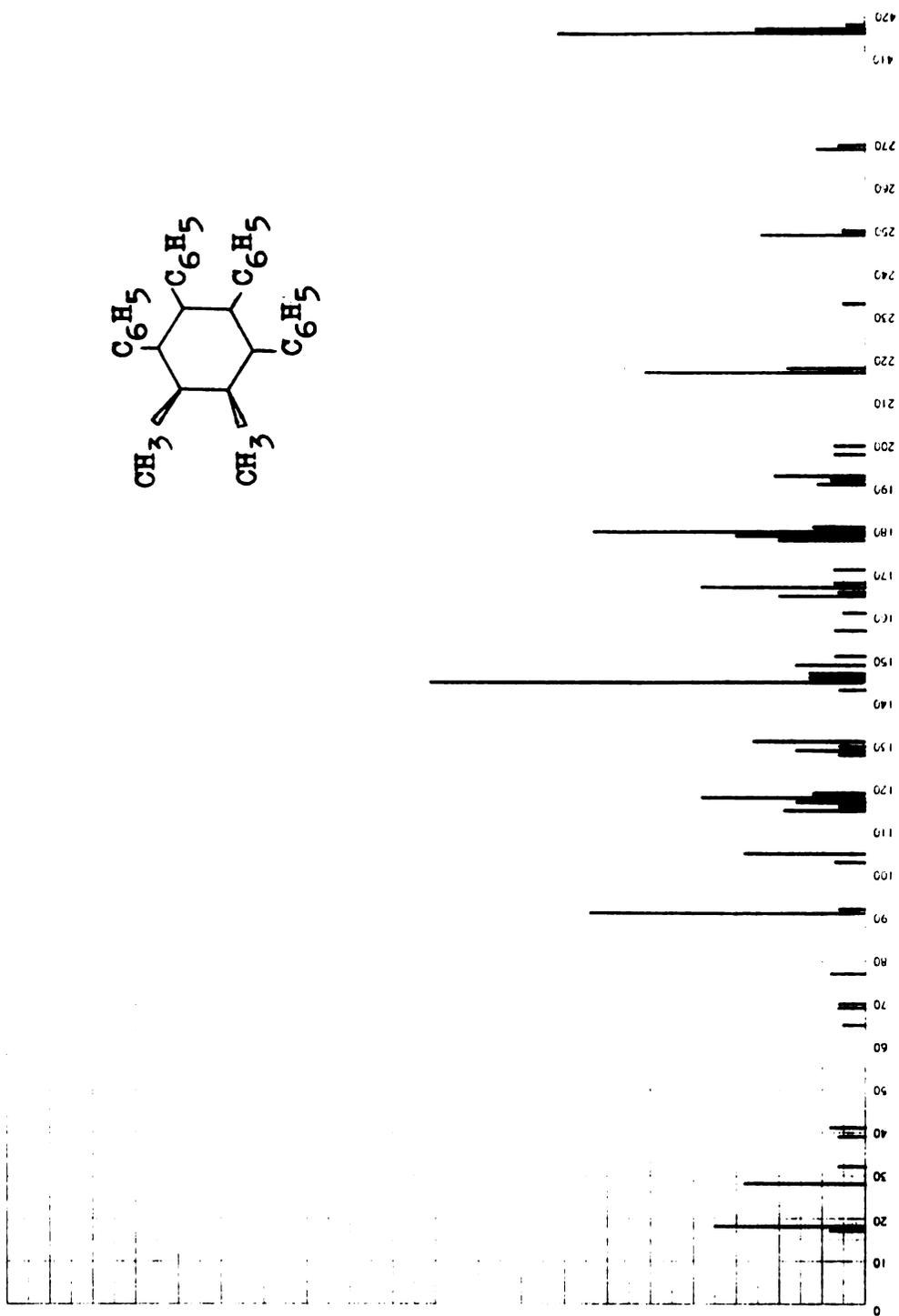


Figure 15. The mass spectrum of compound 8.

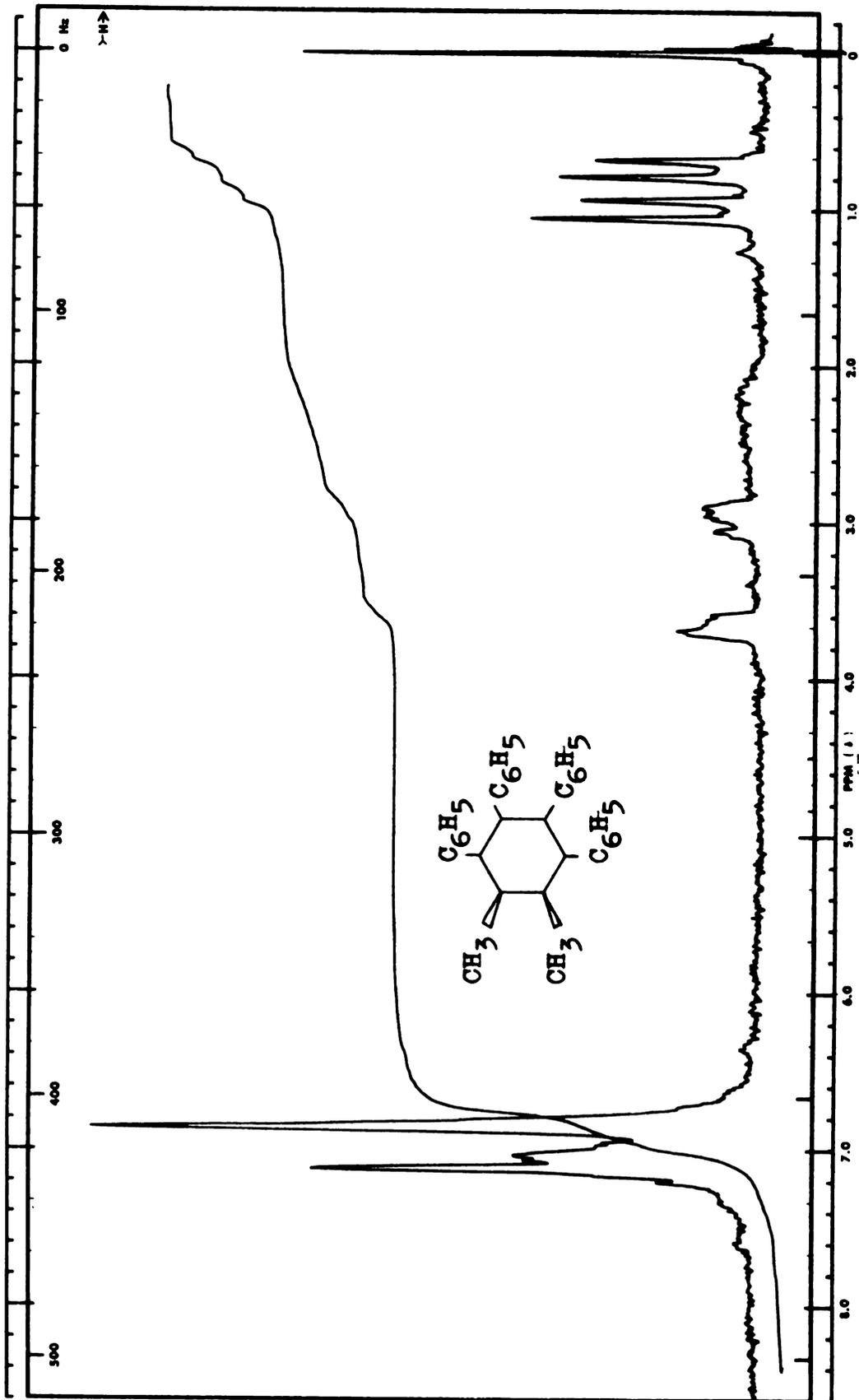


Figure 16. The 60 mc NMR spectrum of compound 8.

Attempted preparation of 1-benzyl-2,3,4,5-tetraphenylcyclohexane (9) or 1-methyl-2,3,4,5,6-pentaphenylcyclohexane (10).

A solution of cinnamyl lithium, prepared by cleavage of cinnamyl phenyl ether (36) with lithium, was reacted, as in the preparation of 5, with 9.0 gm (0.05 mole) of trans-stilbene. The resulting viscous oil would not give a solid product on standing or after trituration with methanol or with pentane and was eluted with chloroform from a silicic acid column as a single broad band.

Attempted preparation of 2,5-diphenyl-3-methylcyclohexene (11).

A solution of allyl lithium was reacted, as in the preparation of 5, with 5.15 gm (0.025 mole) of trans,trans-1,4-diphenylbutadiene. The resulting viscous oil would not give a solid product on standing or after trituration with methanol or with pentane and was eluted with chloroform from a silicic acid column as a single broad band.

Attempted reaction of cyclooctene with triphenylcyclopropylidene phosphorane (37).

2.3 gm (0.005 mole) of triphenyl-3-bromopropyl phosphonium bromide (38) were placed in a 100 ml 3-neck flask equipped with a serum cap, a reflux condenser, and a nitrogen inlet and outlet system; and 1 gm of a 54% sodium hydride suspension, washed free of mineral oil with pentane, was slurried with 25 ml of dry glyme and poured in. The flask was swept with nitrogen, and the contents were heated to reflux under a static nitrogen pressure. One drop of ethanol was injected; and when, after a few minutes, a bright yellow color indicated the presence of ylid, 0.55 gm (0.005 mole) of cyclooctene was injected. Refluxing was continued for three hours during which time the reaction mixture turned a deep mahogany brown. It was then poured into a beaker of ice containing 5 gm of 48% HBr and extracted with ether. (The expected product would, like the starting phosphonium salt, be insoluble in both ether and water; but no third, solid phase separated at this point.) Evaporation of the aqueous layer left a solid residue consisting solely of sodium bromide. The ether layer was evaporated to a wet oil; and this was taken up in methylene chloride, dried, and concentrated. Gas chromatographic analysis of the concentrate showed its only high-boiling, volatile component to be cyclooctene. Thin-layer chromatographic analysis showed the presence of triphenylphosphine and triphenylphosphine oxide.

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