

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### The Fundamental Basis for Cyclopolymerization. VI. An Ultraviolet Spectral Study of Certain Nonconjugated Allylcycloalkenes

George B. Butler<sup>a</sup>; Jan J. Van Heiningen<sup>b</sup>

<sup>a</sup> Center for Macromolecular Science, University of Florida, Gainesville, Florida <sup>b</sup> Department of Chemistry, University of Florida, Gainesville, Florida

**To cite this Article** Butler, George B. and Van Heiningen, Jan J.(1974) 'The Fundamental Basis for Cyclopolymerization. VI. An Ultraviolet Spectral Study of Certain Nonconjugated Allylcycloalkenes', *Journal of Macromolecular Science, Part A*, 8: 7, 1139 – 1174

**To link to this Article:** DOI: 10.1080/00222337408068624

**URL:** <http://dx.doi.org/10.1080/00222337408068624>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## The Fundamental Basis for Cyclopolymerization. VI. An Ultraviolet Spectral Study of Certain Nonconjugated Allylcycloalkenes

GEORGE B. BUTLER and JAN J. VAN HEININGEN\*

Center for Macromolecular Science and  
Department of Chemistry  
University of Florida  
Gainesville, Florida 32611

### ABSTRACT

3-Allylcyclopentene, 4-allylcyclopentene, 3-allylcyclohexene, and 4-allylcyclohexene were prepared in order to compare their UV absorption characteristics with their ability to undergo cyclopolymerization.

The far-UV spectra of the allylcycloalkenes and 4-vinylcyclohexene generally exhibited hypsochromic absorption relative to cyclohexene and 3-propylcyclohexene. This was interpreted to be the result of a destabilizing effect of the double bonds on each other. The spectrum of the previously described 1,4-dimethylenecyclohexane exhibited two long wavelength shoulders which were interpreted as possibly arising from an energy-stabilizing interaction between the double bonds. In addition to the UV spectral study, the monomers were also studied by IR and NMR spectroscopy. No definite ground state interactions between the neighboring double bonds in these monomers were observed in these studies.

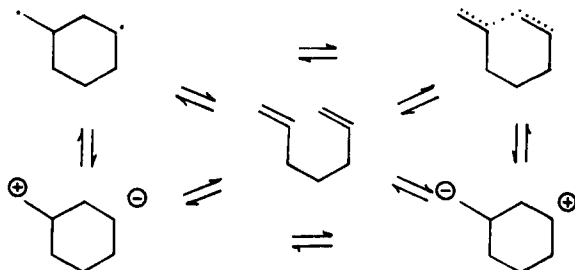
---

\*Taken from the Ph.D. Dissertation of Jan J. Van Heiningen, University of Florida, August 1966.

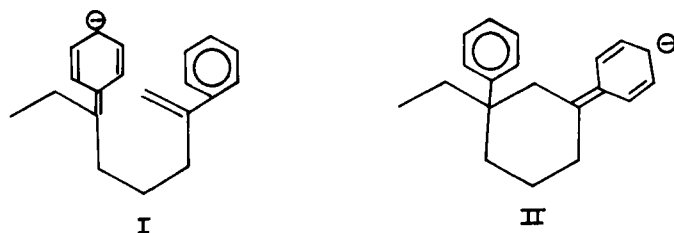
The concept of cyclopolymerization is well established and accepted [1-5]; however, certain aspects of the cyclopolymerization process cannot presently be rationalized with a single mechanism. It was the purpose of this investigation to obtain further experimental evidence which might aid in rationalization of these unexplained observations. For example, probability calculations [6] indicate the maximum monomer concentration of a 1,6-heptadiene which could lead only to cyclic polymer to be 0.01 mole/liter, while there is ample experimental evidence to show that in many cases, monomer concentrations of 5 to 8 moles/liter lead only to cyclic polymer, to no cross-linking, and to no detectable residual double bond.

The most probable steps in the cyclopolymerization process involve 1) initiator attack on the diene to yield a reactive intermediate having a pendant double bond; 2) competition between cyclization according to a cyclization rate constant,  $k_c$ , and linear propagation to a neighboring monomer molecule according to a propagation rate constant,  $k_p$ ; and 3) termination. If cyclization is predominant, the polymer structure will be largely cyclic; however, if linear propagation occurs to any great extent without cyclization, a large amount of pendant double bond will remain on the polymer, a situation which would ultimately lead to extensive cross-linking. Experimental evidence shows that the latter does not ordinarily occur and that the value of  $k_c/k_p$  generally ranges from 5 to 20 moles/liter [5]. However, the activation energy for cyclization,  $E_c$ , in every case studied has been found to be greater than  $E_{11}$ , the activation energy for linear propagation without cyclization [5]. Also, the overall rate of polymerization of typical diolefinic monomers is almost always greater than that of structurally related monoolefins [5].

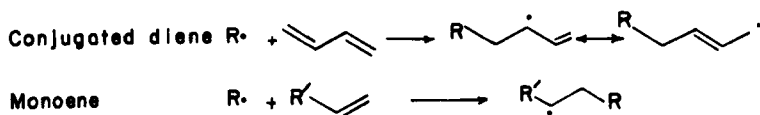
Two basic mechanistic approaches have been made to account for the fact that cyclization is favored over intermolecular propagation. The first emphasizes electronic effects in which Butler suggested that there may be an interaction between the two double bonds [1]. This interaction can be interpreted as excited state or ground-excited state phenomena as represented below. The interaction would render polymerization through both double bonds the more favorable process versus polymerization through either double bond alone. Butler [7] has also suggested that an electronic interaction might exist between



the pendant double bond and the radical generated by the initiator. Marvel and Stille [8] have suggested a similar interaction between an ion generated by the initiator and the pendant double bond. As has been pointed out by Butler and Van Heiningen [9] in a review of non-conjugated interactions of this type, such interactions would be greatly favored in the carbonium ion case, less so in the radical case, and disfavored in the anion case. In the latter case, simple molecular orbital calculations indicate a linear rather than a tricentric transition state to be favored [9]. However, experimental evidence by Field [10] has shown that 2,6-diphenyl-1,6-heptadiene undergoes polymerization by free radical, cationic, anionic, and coordination-type initiation to give in all cases cyclic polymer of essentially the same structure and containing few or no residual double bonds. These results tend to eliminate the necessity of invocation of electronic interactions to account for cyclopolymerization in this case, as theoretical considerations [9] tend to refute the idea that such an interaction could occur in the anionic and coordination-type initiating systems. It should be pointed out, however, that resonance stabilization of the intermediate carbanion could be equally effective through contribution by valence bond Structure II below as by valence bond Structure I for that portion of the population of the species so favorably oriented conformationally. This is particularly true since



Structure II does not require the tricentric transition state referred to above [9]. Presumably, a somewhat related polymerization is that of butadiene by a free radical source. Here the double bonds can interact with each other since they are joined by a sigma bond. Initiation by a radical yields a resonance stabilized intermediate for the diene, but an unstabilized radical for the monoene:



The effect of the second double bond would be to lower the energy of the intermediate radical from the diene relative to that of the

monoene. This is represented above by the two approximately energetically equivalent resonance forms that represent the diene, while only one form exists for the monoene. The ground state energy of the monoene would be lowered somewhat by addition of a second double bond through contributions of the resonance forms  $\ominus\text{-CH=CH-CH=CH}\text{-}\oplus$  and  $\oplus\text{-CH=CH-CH=CH}\text{-}\ominus$ . However, these resonance forms are of significantly higher energy than that of the uncharged structure  $\text{CH}_2\text{=CH-CH=CH}_2$ . They will, therefore, contribute less to the stabilization of the ground state than the corresponding structures did to the transition state. The net result will be a lowering of the overall energetics for the conjugated diene relative to that of the monoene. This can be depicted by the potential energy diagram shown in Fig. 1 [11].

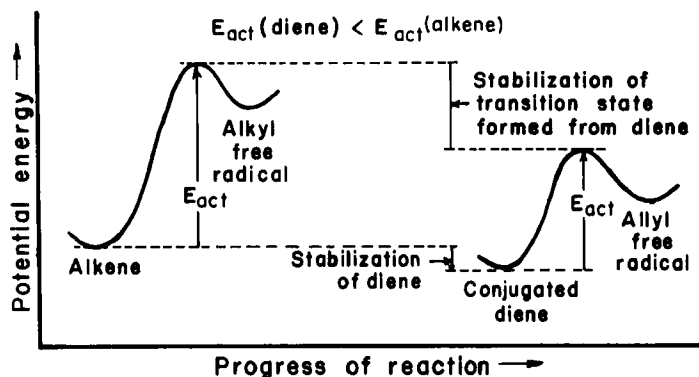


FIG. 1. Energetics of radical-initiated polymerization of a conjugated diene vs an alkene.

These observations are supported by the fact that butadiene polymerizes predominantly by a 1,4-mechanism when initiation is by a free radical source [12]. The vinyl groups which escape polymerization in the polymer do not cross-link until high conversions are reached.

Further consideration of the conjugated diene system permits another possible analogy to be drawn. Addition of hydrogen bromide to 1,3-butadiene by an ionic mechanism leads to a mixture of the 1,2-addition product and the 1,4-addition product, the composition of which depends upon the temperature [11]:



of a cross-linked polymer. These concepts will be developed further in the following discussion.

The second mechanistic approach emphasizes steric factors rather than electronic factors. Gibbs and Barton [5] have noted that the absolute rate constants for propagation and termination, respectively, for methyl acrylate and butyl acrylate favor propagation of the methyl ester by a factor of 52 and termination of the same ester by a factor of 245. They conclude that the pendant butyl group shields the intermediate radical and thus controls both propagation and termination rates in this case. A comparison is made between this case and the reactive intermediate generated from a nonconjugated diene. If the distance of the residual double bond from the reactive site is such that a sterically favorable ring can be formed by the cyclization reaction, cyclization will be the favored course. At the same time, the reactive site is being sterically shielded from attack on a neighboring monomer molecule.

One serious deficiency of the steric-control mechanism is its inability to account for the facts: 1) that the overall rate of polymerization of suitable diolefinic monomers is almost always greater than the reactivity of closely related monoolefins; 2) that certain monoolefins, e.g.,  $\alpha$ -methylstyrene, undergo neither free radical nor coordination-type initiation, while 2,6-diphenyl-1,6-heptadiene readily undergoes both to yield only cyclic polymer [10]; and 3) the magnitude of the rate enhancement referred to in 1) shows little relationship to the severity of steric factors [13]. Butler and Kimura [13] have reported the intramolecular double bond concentration with respect to the neighboring reactive site, when the cyclization step is considered to be pseudo-second order, to be  $>20.4$  moles/liter, a physically impossible situation since the concentration of liquid ethylene at its boiling point is only 21.8 moles/liter. Carlsson and Ingold [14] have indicated such hypothetical concentrations to be as high as 100 moles/liter.

If the electronic interaction theory [1, 7] is correct, evidence for these interactions may be available through UV spectroscopy. Using butadiene again as an example, its UV spectrum compared to ethylene is as given in Table 1.

TABLE 1

Compound	$\lambda_{\max}$ (nm)	$\epsilon$	Ref.
$\text{CH}_2=\text{CH}_2$	171	15,530	20
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	217	20,900	20

A single double bond absorbs at 171 nm. Placing a second double bond in conjugation with the first produces a bathochromic shift of 46 nm and a somewhat less than doubling of the extinction coefficient. If the double bonds in the nonconjugated dienes under consideration are interacting, detection of this interaction should be possible through UV absorption spectroscopy. A bathochromic shift, the appearance of a new transition or a disproportionate change in intensity on going from the monoene to the diolefin, would signal the fact that an interaction was occurring.

It was the purpose of this study to synthesize suitable nonconjugated olefins, to investigate their UV spectra, and to study their polymerization characteristics in an effort to correlate any spectral anomalies with the cyclopolymerization characteristics of the dienes.

The first examination into this theory was made by Butler and Brooks [15]. The authors synthesized *cis* and *trans*-1,3,8-nonatriene and studied the UV spectral characteristics of these and other related olefins. These compounds all showed bathochromic shifts from the 222 nm predicted by Woodward's rules [16]. It is also obvious that the  $\epsilon$  values are not additive. An isolated double bond is essentially transparent in the 220 to 230 nm region. The addition of the isolated third double bond should cause no change in the extinction coefficient which is seen not to be the case. Later work by Butler and Raymond [17] showed that 1,3-nonadiene absorbed at 226.5 nm ( $\epsilon = 27,600$ ), indicating little, if any, bathochromic shift for the 1,3,8-nonatrienes, but lack of additivity in the  $\epsilon$  values.

Marvel and Hwa [18] found that myrcene could be polymerized by cationic catalysis into cyclic, soluble polymers. Other initiating systems yielded only the linear 1,4-polymer. Butler and Brooks [15] found that *cis*-nonatriene gave only insoluble polymer while the *trans* isomer did yield 50% soluble polymer.

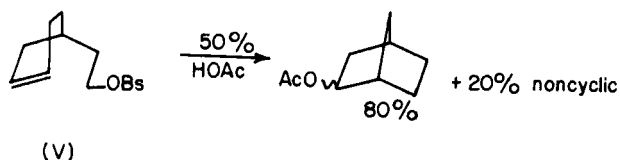
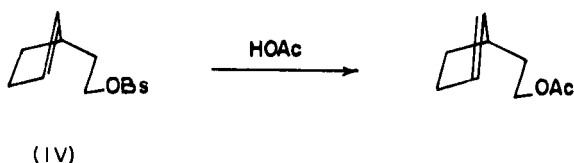
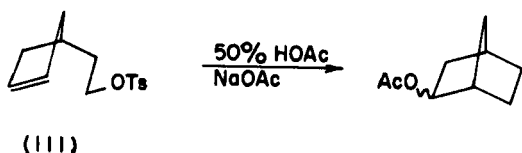
Butler and Raymond [17] investigated several tetraenes which contained two pairs of conjugated systems situated in such a manner that an electronic interaction might occur and compared their spectra with suitable model dienes. In all cases the  $\epsilon$  values were non-additive. 1,3,6,8-Nonatetraene exhibited a bathochromic shift of 10.6 nm and also new absorptions at 261.0 and 272.1 nm. This monomer, of the three studied, produced the poorest yield of the polymer [19]. The highest conversion obtained was 17% of which only 10 to 50% was soluble. The other tetraenes, 1,3,9,11-dodecatetraene and 3,6-dimethylene-1,7-octadiene, when polymerized to 50% conversion yielded 50 to 75% soluble polymer.

Neither of the foregoing investigations conclusively establish that electronic interactions are in effect nor do they satisfactorily correlate with cyclopolymerization tendencies. It would seem more desirable to study less complicated systems such as nonconjugated diolefins. With the recent availability of instruments capable of searching the far-UV, research into this area is now possible.



Biallyl (1,5-hexadiene) is known not to show a bathochromic shift in the UV region [20] although it can be polymerized to cyclic polymers [21]. Since the diene has many possible conformations not favorably aligned for such interactions, other systems which have greatly reduced modes of freedom were designed for synthesis and study.

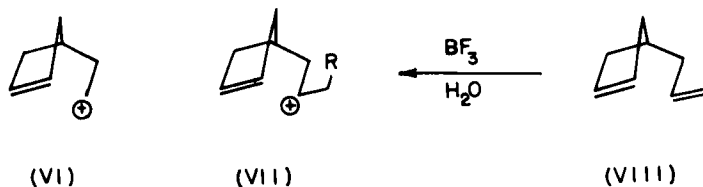
A series of compounds was envisioned from the solvolytic cyclization studies of Bartlett [22], Clossen [23], and Winstein [24]. Bartlett found that solvolysis of 4-cyclopentenylethyl tosylate (III) in acetic acid gave a product which was 92% cyclic. Clossen found that when the isomeric 3-cyclopentenyl brosylate (IV) was solvolized,



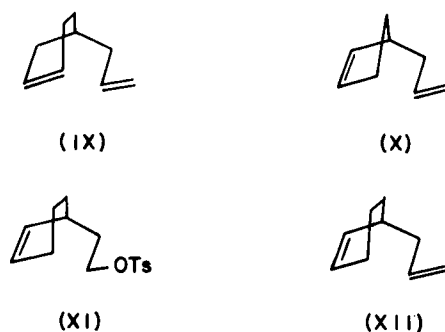
no cyclic material was obtained. In a similar system, Winstein [24] noted that 4-cyclohexenylethyl brosylate (V) gave 80% cyclic products.

Based on the ready cyclization tendencies of Compounds III and V, similar systems for polymerization studies were prepared. The work of Bartlett [25] had established that the reaction occurred by participation of the double bond during solvolysis. Intermediate VI can be considered the reaction intermediate. This ion can be closely approximated by Ion VII which can be considered to form from the cationic initiation of polymerization of 4-allylcyclopentene (VIII). Similarly, the other solvolized systems may be approximated by 4-allylcyclohexene (IX) and 3-allylcyclopentene (X). The unsynthesized 3-cyclohexenylethyl tosylate (XI) suggested the synthesis of 3-allylcyclohexene (XII).

The ready cyclization of the substituted ethyl tosylates suggests that



the two double bonds may have a significant chance of interaction with one another and of yielding high percentages of cyclopolymer.



The synthetic objectives of this investigation involved the synthesis of 3-allylcyclopentene (X), 4-allylcyclopentene (VIII), 3-allylcyclohexene (XII), and 4-allylcyclohexene (IX) as well as suitable model compounds. In addition, 1,4-dimethylenecyclohexane (XIII) along with model compounds methylenecyclopentane and methylenecyclohexane were synthesized.

## RESULTS AND DISCUSSION

### Syntheses Related to Monomer Preparations

1,4-Dimethylenecyclohexane was synthesized by the method of Ball and Harwood [26] and was considered to be an interesting subject for UV analysis. The compound has also been reported to cyclopolymerize.

The model compounds in this series were methylenecyclohexane and methylenecyclopentane. The former compound was synthesized by the well-established procedure of Wittig [27] using Corey's [28] modification. Methylenecyclopentene and (later) methylenecyclohexane were purchased from commercial sources.

The syntheses of the four monomers suggested by solvolytic experiments are all similar since they involved Grignard coupling reactions and unsaturated halocycloalkanes.

Bartlett and Rice [29] reported the synthesis of 4-bromocyclopentene in 1963. Since the authors' publication, there have appeared several notices on the hazardous nature of this reaction [30]. The reaction was run successfully several times with yields varying from 9 to 10.5%. 4-Allylcyclopentene was prepared by the coupling reaction of the Grignard reagent from 4-bromocyclopentene and allyl bromide. Following the completion of this work, Bartlett and Sargeant [31] reported the same synthesis.

The isomeric 3-allylcyclopentene was prepared from known 3-chlorocyclopentene by coupling with allylmagnesium chloride, prepared according to the method of Kharasch and Reinmuth [32].

3-Allylcyclohexene was synthesized by coupling 3-bromocyclohexene with allylmagnesium chloride.

4-Allylcyclohexene was synthesized by coupling the Grignard reagent of 4-chlorocyclohexene with allyl bromide. The structures of the compounds were confirmed by their IR, near-IR, and NMR spectra.

Two compounds were needed as models for the UV spectral studies: allylcyclohexane and 3-propylcyclohexene. Allylcyclohexane was synthesized by coupling cyclohexylmagnesium bromide and allyl bromide through a modification of the procedure of Resseguier [33]. 3-Propylcyclohexene was synthesized by coupling 3-bromocyclohexene and propyl bromide following the procedure of Berlande [34].

### Ultraviolet Spectra of the Monomers

The UV light absorption of a molecule measures the energy necessary to promote an electron from the ground state to an excited state. The energy difference between these two states is equal to the following relationship:

$$\Delta E = E_{\text{E.S.}} - E_{\text{G.S.}} = h\nu = hc/\lambda$$

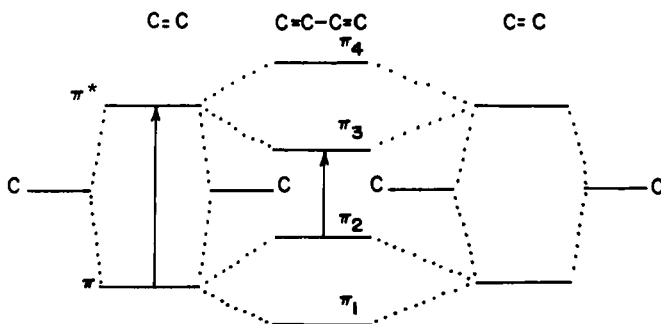
where E is the energy of the state in question, h is Planck's constant, c is the speed of light, and  $\lambda$  is the value of the wavelength of light corresponding to this energy difference. It is seen that the energy difference is inversely proportional to the wavelength of absorption. A review of nonconjugated chromophoric interactions in the UV region has been published by Butler and Van Heiningen [9].

The UV absorption of olefins represents the excitation of an electron in the highest energy occupied orbital to the lowest unoccupied orbital. These orbitals are respectively, the  $\pi$  and  $\pi^*$  orbitals. The UV absorption is then referred to as a  $\pi \rightarrow \pi^*$  transition.

Nonconjugated diolefins, such as 1,5-hexadiene, generally absorb in the region of 170 to 200 nm depending on the substitution pattern, geometry of the double bond, etc. These wavelengths correspond to

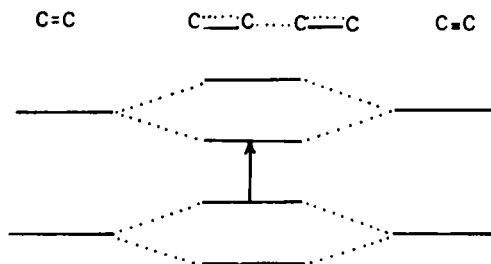
energies of 168 and 142 kcal/mole, respectively. Conjugated dienes, such as butadiene, absorb in the region from 217 to 290 nm depending also on substitution, geometry, etc. These wavelengths correspond to energies of 132 and 99 kcal/mole, respectively.

A molecular orbital description of the bonding that takes place in butadiene can be represented by the molecular orbital diagram [16]:



The bathochromic shift observed for the conjugated diene results from a mixing of the  $\pi$  orbitals of the isolated  $C=C$  groups. The lowest unoccupied orbitals and the highest occupied orbitals,  $\pi_3$  and  $\pi_2$ , are seen to have been moved closer together, thus decreasing their energy difference.

For a system containing two olefinic groupings, not formally conjugated, a similar energy diagram can be constructed:



Depending on such factors as the amount and geometry of overlap of the  $\pi$  electron systems, a somewhat similar situation to that in butadiene should exist [35]. The energy of the resultant transition should be inversely proportional to the amount of overlap in the first approximation [36]. Consequently, as interaction occurs, it would be expected that the absorption maximum would shift to longer wavelengths.

This reasoning leads one to postulate bathochromic shifts or new, longer wavelength absorption bands as evidence for interactions. It also seems reasonable that if there were no interaction, the intensities of the component parts of the diolefin should be exactly double that in the monoolefin. Any deviation from the expected intensity might be evidence for interaction. It must be pointed out, however, that the experimental  $\epsilon$  value is quite susceptible to procedural errors and also to stray light errors in the far-UV [37]. Due concern must be shown for any small abnormalities since they may reflect only experimental error.

The effect of solvents on the  $\pi \rightarrow \pi^*$  transition in olefins is a well recognized but poorly understood phenomenon. A concise summary of the problem is contained in the classic book in UV spectroscopy by Jaffe and Orchin [16]. Two effects are of importance in this study. First, nonpolar solvents produce spectra which closely resemble those of the vapor. In such solvents as heptane and isooctane, vibrational fine structure is visible as it is in the vapor spectrum. More polar solvents tend to dampen the vibrations of the solute through solvation. Such solvents as acetonitrile and ethanol will produce spectra free of vibrational peaks in many cases.

A second effect of solvent polarity is shown on the maxima. In systems such as  $C=C$  and  $C=O$  the excited state can be represented by large contributions from highly polar structures like  $\overset{\oplus}{C}-\overset{\ominus}{C}$  and  $\overset{\oplus}{C}-\overset{\ominus}{O}$ . Polar solvents facilitate the electronic excitation by solvation of the excited state more than that of the ground state. Thus bathochromic shifts are found on changing solvent polarity from the least polar to the more polar.

The UV spectra of 1,4-dimethylenecyclohexane, methylenecyclohexane, and methylenecyclopentane are listed in Table 2. Methylenecyclohexane was selected as the closest possible model for the diolefin. The five-membered ring analog was investigated to determine the effect of ring strain on the absorption.

1,4-Dimethylenecyclohexane exhibited a maximum at 198.2 nm and two longer wavelength shoulders at approximately 203 and 208.5 nm (isooctane). Figure 3 shows the experimentally determined curve. This diene displayed the expected small bathochromic shift on going to the more polar solvent, 95% ethanol. The polar solvent also caused a decrease in intensity of the absorption. This was a general phenomenon with all the olefins. All the monomers were found to obey Beer's law (absorption proportional to concentration).

It seems clear that increasing ring strain shifts the absorption to longer wavelengths. Methylenecyclohexane absorbs at 191 nm while the five-membered ring analog absorbs at 195 nm. Introduction of a second  $sp^2$  carbon into the six-membered ring, as in 1,4-dimethylenecyclohexane, probably is the reason for the shift to 198 nm.

The shoulder present in the six-membered ring olefins presents

TABLE 2. Ultraviolet Spectra 1,4-Dimethylenecyclohexane and Related Compounds

Compound	Solvent	$\lambda_{\max}$ (nm)	$\epsilon$
1,4-Dimethylene cyclohexane	Isooctane	198.2	21,000
		202.8 (sh)	18,500
		208.6 (sh)	10,300
	95% Ethanol	198.6	19,500
		203.3 (sh)	17,200
		208.9 (sh)	9,600
Methylenecyclo- hexane	Isooctane	191.3	11,700
		197.5 (sh)	9,200
	95% Ethanol	191.8	10,900
Methylenecyclo- pentane	n-Heptane	195.4	8,800
	95% Ethanol	195.3	7,700

a problem in interpretation. The removal of the shoulder in methylenecyclohexene by a polar solvent suggests the blurring out of a vibrational band. If this were so, it would be necessary to ascertain whether the electronic transitions are from excited vibrational levels in the ground electronic state to approximately equal energy vibrational levels in the first electronic excited state. An alternative explanation would be the excitation from the lowest lying vibrational level of the ground electronic state to the excited vibrational levels in the first electronic excited state.

Evidence which distinguishes between these possibilities or suggests some other cause for producing the shoulders was not available. It is usually assumed that electronic transitions occur from the ground vibrational state since at room temperature a preponderance of organic molecules are in that state [16]. A crude energy calculation was made to determine the energy represented by the difference between the  $\lambda_{\max}$  and the approximate position of the first shoulder.

The difference of  $1651 \text{ cm.}^{-1}$  was comparable to the C=C vibrational stretching frequency in the IR. However, a Boltzmann distribution  $\{n_1/n_2 = \exp[-(e_1 - e_2)/kT]\}$  indicated that for this energy difference, only 34 out of 10,000 molecules would be in this excited vibrational state. This was inconsistent with the magnitude of the shoulder, even after subtracting out the  $\pi \rightarrow \pi^*$  absorption.

A careful consideration of the vibrational bands in benzene reveals that they were symmetrically dispersed about the envelope [16].

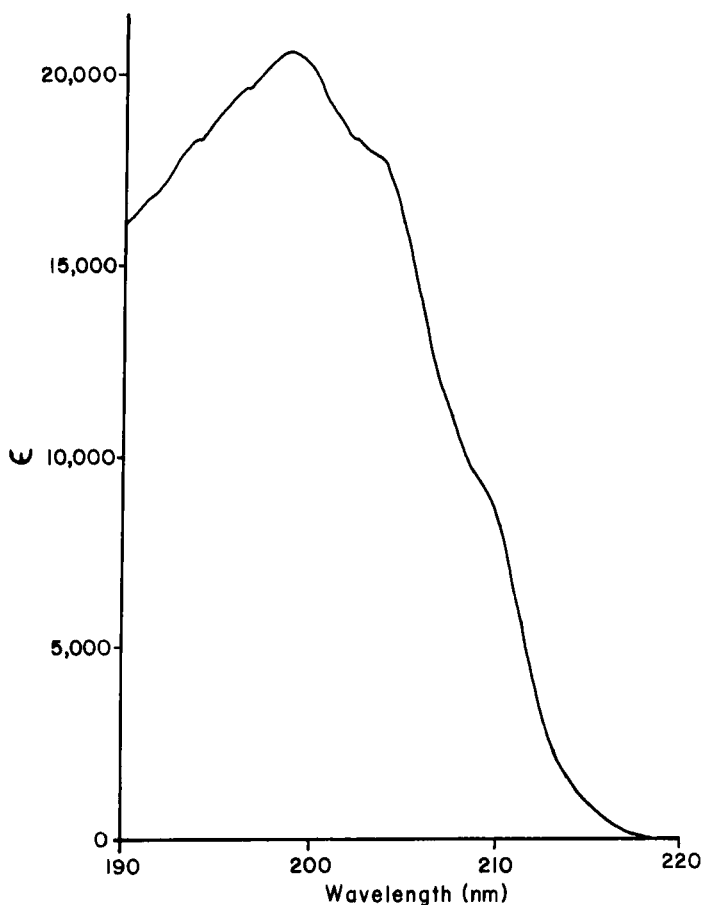


FIG. 3. Absorption curve of 1,4-dimethylenecyclohexane in isoctane.

Investigation of the high energy side of the  $\pi \rightarrow \pi^*$  band in methylenecyclohexane was obscured because of the onset of ionization effects. Hence the correlation with the vibrational spectra of benzene was impossible.

A conclusion must be reached that the assignment of the shoulder in methylenecyclohexane was impossible with the present data. A temperature study and computer analysis of the absorption curves would be helpful.

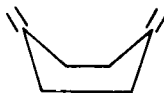
There was double the problem in 1,4-dimethylenecyclohexane due

to the presence of the two shoulders. Again assignment of the shoulders to a particular cause was impossible. The energy separation between the transitions was in the region of  $1200\text{ cm}^{-1}$ . A Boltzmann distribution indicated a low population for excited vibrational states in the ground electronic state (0.0013). A second vibrational level should be even more sparsely populated. Here it was difficult to determine if the long wavelength shoulder could arise from this low population. The high energy side of the absorption peak was also obscured by ionization processes.

It must be again concluded that without further investigation, a definite assignment could not be made. There was the possibility of an interspatial interaction between the double bonds leading to a new, longer wavelength transition. The fact that two shoulders were found could possibly indicate that 1,4-dimethylenecyclohexane existed in several conformations within which interactions of different magnitudes were occurring. This must be considered as speculation since no definite assignments were possible.

A temperature study was attempted on the monomer by NMR spectroscopy. The diolefin was studied as the neat liquid over a temperature range from 25 to  $-40^\circ\text{C}$  (freezing point). No evidence of peak broadening or migration was found.

Simple Hückel molecular orbital calculations [38] were performed on the diolefin. The molecule was assumed to be in the boat conformation (XIII) and to possess normal bond lengths and angles. Calculations indicated that the bow-stern distance of the ring was



(XIII)

2.58 Å. Extrapolated  $\sigma,\sigma$  and  $\pi,\pi$  overlap integrals from Kopineck [39] were used for the noncoplanar orbitals.

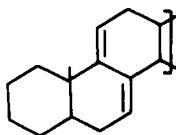
A value of  $0.48\beta$  was obtained for the resonance integral between the olefinic groups. Using this value, the following energy diagram was obtained through the use of the standard molecular orbital calculating procedure:

$$\begin{array}{r} \text{_____} \alpha - 1.27 \beta \\ \text{_____} \alpha - 0.79 \beta \\ \text{xx} \alpha + 0.79 \beta \\ \text{xx} \alpha + 1.27 \beta \end{array}$$

This value of  $\beta$  indicated a delocalization energy of  $0.11\beta$  for the nonconjugated diolefin. This is to be compared with the delocalization



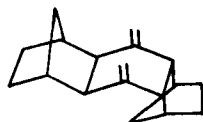
energy of butadiene ( $0.47 \beta$ ). A delocalization energy which is 24% that of butadiene seems large. If Woodward's rules are used loosely and applied to this system, a calculated  $\lambda_{\max}$  of 245 nm is obtained. A somewhat similar system (XIV) also absorbs at 245 nm [16].



(XIV)

A transition representing 24% of the delocalization energy of butadiene would be expected to occur at 207 nm ( $0.24 \times 50$  nm) using methylenecyclopentane as the model. This calculation assumes that a linear relationship exists between  $\lambda_{\max}$  and the delocalization energy. The result conveniently falls in the region of the shoulders but it is probably fortuitous.

Orloski [40] has investigated the analogous system where the 1,4-dimethylenecyclohexane system (XV) is locked into the boat conformation.



(XV)

$\lambda_{\max}$ heptane
192, 198 nm
monoolefin, 200 nm

Figure 4 reproduces Orloski's UV curves for the mono and diene. These data were interpreted as arising from nonconjugated interactions between the olefin groups. It was noticed that the diolefin absorbed at higher intensity at longer wavelengths than the monoolefin. This was interpreted as being caused by a new transition at about 210 nm which was submerged by the main  $\pi \rightarrow \pi^*$  transition at 200 nm. The transition at 198 nm was also ascribed to a new absorption.

Orloski [40] also found new transitions in the spectra of Compounds XVI and XVII. Aside from several smaller shoulders, both compounds exhibited a new peak at shorter wavelength and a shoulder at longer wavelength than that of the corresponding monoolefin. The data for the new transitions are listed in Table 3.

Orloski [40] concludes that the interaction between the olefinic

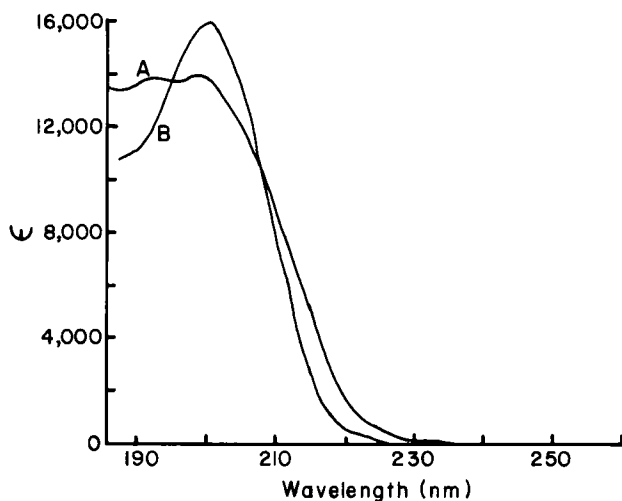
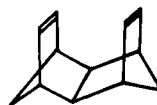


FIG. 4. UV absorption spectra of XV (A) and the corresponding monoolefin (B) [40].



(XVI)



(XVII)

groups has produced a higher and a lower energy transition. The lower energy absorption is similar to the  $\pi_2 \rightarrow \pi_3$  transition in butadiene.

TABLE 3

Compound	New short wavelength band (nm)	Old $\pi \rightarrow \pi^*$ band (nm)	New long wavelength band (nm)
XV	192	198	~215
XVI	187	193	216 (sh)
XVII	192	195	210 (sh)

Evidence for a new high energy band could not be found in the spectra of 1,4-dimethylenecyclohexane, unless it is assumed that the main transition corresponds to the first shoulder. This does not seem likely.

The evidence indicates that an interaction might be occurring in 1,4-dimethylenecyclohexane. Possibly this work, coupled with that of Orloski [40], establishes that nonconjugated diolefins can have overlap of their electron systems to produce transitions similar to those in butadiene and other conjugated systems.

A second series of investigations dealt with the isomeric 3- and 4-allylcyclohexene and related compounds. Table 4 lists the spectral data obtained for these olefins. These compounds all showed a bathochromic shift and a reduction in intensity on changing from heptane to acetonitrile. All the monomers were found to obey Beer's law.

The most surprising feature of these monomers was that all of the diolefins absorbed at the same or shorter wavelength than the model compounds. The first model selected was cyclohexene. It was soon noticed that the diolefins were not shifting bathochromically but hypsochromically from this olefin. Since all of the diolefins are substituted cyclohexenes, it was thought desirable to synthesize 3-propylcyclohexene as a model. This compound, however, exhibited a bathochromic shift over that which was found in cyclohexene.

There must, therefore, be some unusual effect in the operation to explain these strange results. If the olefins had been interacting, a bathochromic shift would have been predicted. The fact that 4-allylcyclohexene absorbs at shorter wavelength than either cyclohexene or 3-propylcyclohexene clearly indicates that another factor is in operation.

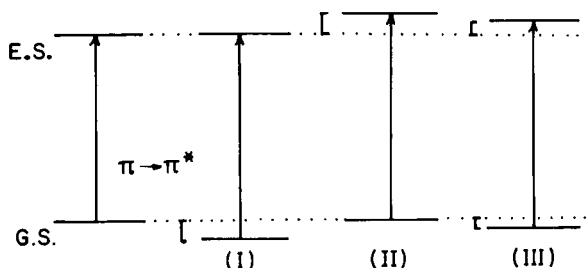
TABLE 4. Ultraviolet Absorptions of Some Cyclohexenyl Compounds

Monomer	Absorption maximum (nm)	
	n-Heptane ( $\epsilon$ )	CH <sub>3</sub> CN ( $\epsilon$ )
4-Vinylcyclohexene	179.1 (19,800)	180.0 (17,500)
4-Allylcyclohexene	179.1 (21,500)	179.8 (19,500)
Allylcyclohexane	180.5 (11,500)	181.1 (10,500)
3-Allylcyclohexene	181.8 (18,800)	183.0 (17,600)
Cyclohexene	181.8 (9,100)	183.1 (8,400)
3-(n-Propyl)cyclohexene	186.1 (9,300)	186.4 (8,700)

It must be remembered that small effects in the far UV are undoubtedly due to many contributions. The maxima listed in Table 4 are actually the results of the different olefinic components absorbing throughout the solution. The observed  $\lambda_{\max}$  is, in fact, the weighted average of the transition probabilities of the two types of double bonds, cis and vinyl. For example, the absorption of 3-allylcyclohexene (181.8 nm) could arise from a mixture of allylcyclohexane (180.5 nm) and 3-propylcyclohexene (186.1 nm).

What will be attempted is an explanation of the hypsochromic shifts observed in 4-allylcyclohexene and 4-vinylcyclohexene. It does not seem possible to explain a hypsochromic shift by averaging the two longer wavelength absorptions. A tentative explanation will be offered which will have to suffice until a greater understanding of far-UV spectroscopy is obtained.

To explain a hypsochromic shift, there can be but three general explanations. These possibilities are outlined here in terms of energy changes on the ground and/or excited states:



The first possibility is to lower the ground state (G.S.) energy or to lower it more than the excited state (E.S.) energy is lowered. A second alternative is to raise the energy of the E.S. or raise it more than the amount G.S. is raised. Finally, the E.S. could be raised while lowering the G.S. energy. To distinguish between these possibilities is rather difficult. Evidence to be presented in this section on other physical methods reveals little or no G.S. stabilization. On the basis of this, hypsochromic effect I can be eliminated. The choice between II and III appears to be impossible to resolve.

The only reasonable explanation appears to be through a combination of electron donating (+I) and electron withdrawing (-I) inductive effects. It is known from a series of ionization potential (I.P.) measurements by Price [41] that alkyl groups stabilize both the ground and excited states. His calculations indicate that the effect of the methyl is to stabilize the excited state 7 to 8 times more than the ground state. This explains the decrease in I.P. with alkyl substitution.

A physical description for this effect was explained by the removal of an electron which leaves a positive hole. This hole polarizes the alkyl groups such that the effective charge is dispersed throughout the molecule. It would seem reasonable that -I groups would destabilize the ion, and destabilize it more than the ground state. Applied to far-UV spectroscopy, the electron is actually not removed from the molecules but it is excited into a  $\pi^*$  orbital which is, however, further away from the molecule than the  $\pi$  bond. Therefore, a partial positive hole might be considered to be left by the excitation.

Very little work has been done on purely inductive effects on UV transitions. This is principally because it is extremely difficult to separate inductance and resonance effects. A few examples though, are available. Filler et al. [42] have found that substitution of the strongly electron withdrawing  $\text{CF}_3$  group on trans-cinnamic acids leads to the hypsochromic absorptions listed in Table 5.

TABLE 5

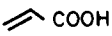
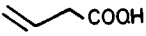
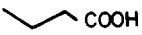
Substituent	$\lambda_{\text{max}}$ (nm)
H	272
o- $\text{CF}_3$	265
m- $\text{CF}_3$	263
p- $\text{CF}_3$	267

Price et al. [43] have found that the CHO,  $\text{CF}_3$ , and CN groups all increase the I.P. of aromatics. He interprets this as mainly a G.S. effect.

Although it is not clear whether inductive effects are mainly a G.S. or E.S. effect, it is clear that something similar to this must be occurring in this allylcyclohexene series. The relative effects of vinyl and allyl groups can be compared by their effects on  $\text{pK}_a$  determinations. The relative -I effect of the vinyl is revealed by data by Brown [44] (Table 6).

The inductive effect of the vinyl is obvious from the comparison of 4-vinylcyclohexene (179.1 nm) and cyclohexene (181.8 nm). Here the vinyl has caused a hypsochromic shift, presumably through destabilization of the excited state. The fact that 3-allylcyclohexene absorbs at 181.8 nm, the same as that for cyclohexene, indicates that the +I effect of the allyl balances out the -I effect of the vinyl. The +I effect of the propyl is indicated by the bathochromic shift of 4.3 nm from cyclohexene.

TABLE 6

Group	Acid	pK <sub>a</sub>
Decreasing -I ↓	Vinyl 	4.25
	Allyl 	4.35
	Propyl 	4.82

The lower value of 179.1 nm for 4-allylcyclohexene relative to the 181.8 nm value for 3-allylcyclohexene reflects the fact that the +I effect of the allyl has diminished with distance while the -I effect of the vinyl has not. This seems reasonable if one postulates a field effect for the induction caused by the vinyl group. Bartlett and co-workers [31, 45] have shown that the double bond is rate retarding in various 1,5 and 1,6 unsaturated tosylates by about 0.7 where no cyclic products were formed. This indicates that the double bond is acting in an interspatial manner rather than through a chain effect.

The compounds appear to be additive with respect to their extinction coefficients. It therefore appears that there is no evidence for interaction in this series.

The third group of monomers, the allylcyclopentenes, behave in a similar manner. Table 7 lists the absorption data for these monomers. Both diolefins are positioned hypsochromically with respect to cyclopentene. This result again seems to be explained by the destabilization effect of the double bonds on one another. In both cases the allyl effect is overridden by the vinyl group. This was not so in the case of 3-allylcyclohexene in which they were about equal. Possibly the difference is that in the five-membered ring analog, a closer approach is allowed between the two double bonds, hence magnifying the field effect. Drieding models confirm that the cyclopentene geometry allows this closer approach.

Finally, Table 8 contains the data for two linear olefins. The diene appears to be bathochromically shifted by 1 nm. Unfortunately, the model compound, 1-heptene, was not available. Another CH<sub>2</sub> unit might decrease this shift so that it would be too small to certify as being real since the accuracy of the instrument is just 0.4 nm. Further work is necessary in this area.

The evidence indicates that an interaction might have been observed in the semiflexible 1,4-dimethylenecyclohexane case. However, the monomers based on solvolytic ring closure experiments behaved generally as if inductive field effects of the second double bond were the most important. The diolefins appeared to interact, but in a

TABLE 7. Ultraviolet Absorption of Some Cyclopentenyl Compounds

Compound	n-Heptane		CH <sub>3</sub> CN	
	$\lambda_{\max}$ (nm)	$\epsilon$	$\lambda_{\max}$ (nm)	$\epsilon$
4-Allylcyclopentene	180.0	18,600	180.6	16,900
3-Allylcyclopentene	182.3	17,400	182.7	15,400
Cyclopentene	184.1	9,600	184.8	7,900

TABLE 8. Ultraviolet Absorption of Some Linear Olefins

Compound	n-Heptane		CH <sub>3</sub> CN	
	$\lambda_{\max}$ (nm)	$\epsilon$	$\lambda_{\max}$ (nm)	$\epsilon$
1,6-Heptadiene	179.0	23,600	181.1	21,700
1-Hexene	178.8	12,800	180.4	11,400

manner opposite to that which was predicted. No explanation is immediately apparent for why this should be so. An orientation effect of one double bond on the other might be important. That is, unless the double bonds are overlapping in a  $\sigma$  or  $\pi$  fashion, they are not stabilizing but destabilizing. Further work into this area is obviously necessary.

Table 9 contains the UV spectra of the monomers covering the region from 210 to 300 nm in which each monomer showed a small but significant absorption.

Olefins exhibit extremely weak absorptions ( $\epsilon$  10) in this region. The shelf usually extends from about 210 to 300 nm depending on the type of olefin. For some time, absorptions were believed to be caused by a singlet to triplet excitation of the  $\pi$  electron [46]. This would be a forbidden transition since spin changes on excitation are not allowed. This singlet to triplet transition was later identified as occurring at about 300 nm by Reid [47] and Evans [48]. This again left the origin of the shelf transition unexplained as it is still today. Berry [49] has attempted to explain it in terms of a  $n-\pi^*$  analogy to formaldehyde.

TABLE 9. Ultraviolet Absorptions of the Monomers above 210 nm

Monomer	n-Heptane		95% EtOH	
	$\lambda_{\max}$ (nm)	$\epsilon$	$\lambda_{\max}$ (nm)	$\epsilon$
4-Allylcyclopentene	222.5	30.8 sh	228.75	35.1 sh
	259.0	2.0 sh		
3-Allylcyclopentene	250.0	4.0 sh	230.3	25.9 sh
	277.5	1.7 sh	268.8	2.5 sh
Cyclopentene	225.0	18.8 sh	225.5	47.2
	237.1	5.6 sh		
	242.1	4.8 sh	260.0	5.1
	256.8	3.5 sh		
	280.0	2.0 sh	287.8	3.1
1,4-Dimethylenecyclohexane	234.0	7.6 sh	234.0	8.5 sh
	265.4	2.2	265.0	2.4
	268.3	1.9	268.1	2.1
	272.1	1.5		
	273.9	1.5	272.9	1.6
Methylenecyclohexane	233.8	2.6 sh		
Methylenecyclopentane	236.0	4.4 sh		
	242.5	2.9 sh		
	248.3	1.5 sh		
	256.3	0.8		
	260.3	0.4		
4-Vinylcyclohexene	258.5	2.7 sh	228.3	14.4 sh
	266.3	3.2	268.4	3.4 sh
	275.0	2.2 sh		
4-Allylcyclohexene	221.0	9.5 sh	222.6	3.5 sh
	258.6	4.4 sh		
	261.0	4.8 sh		
	264.3	5.7		
	267.3	5.3	267.3	5.4 sh
	270.5	6.9	271.6	5.8
	274.0	4.1 sh		
277.3	6.1	278.4	4.4 sh	
3-Allylcyclohexene	226.3	70.9 sh	230.0	77.9 sh
	242.8	17.1		
	248.5	15.2	248.5	19.8 sh
	254.5	14.8	254.1	16.0
	258.0	13.7		

(continued)



TABLE 9 (continued)

Monomer	n-Heptane		95% EtOH	
	$\lambda_{\text{max}}$ (nm)	$\epsilon$	$\lambda_{\text{max}}$ (nm)	$\epsilon$
3-Allylcyclohexene (cont'd)	260.9	14.4	260.5	14.2
	264.3	14.6	264.8	13.6
	267.8	13.1	268.3	13.4
	270.6	15.4	271.4	13.3
	273.6	10.5 sh		
	277.3	13.1	279.8	9.8 sh
3-(n-Propyl)cyclohexene	267.9	3.7		
	264.5	3.6		
	261.3	4.4		
	258.8	4.4		
	254.8	4.3		
	252.8	4.5		
	247.5	5.2 sh		
Cyclohexene	268.8	0.3 sh	260	0.2 sh
1,6-Heptadiene	No max or shoulder		No max or shoulder	
	max of 220	0.37	max of 220	0.45
Allylcyclohexane	225.0	3.9	225.0	2.9
	No shoulder		No shoulder	
1-Hexene	225.0	0.3		
	No shoulder			
	238.8	0.1 sh		

Absorptions with such low values surely will be sensitive to impurities. Potts [50] has noted that oxygen affects these bands. Because of the uncertainty in the origin and the value of these absorptions, they will be reported but not discussed. One interesting feature is present. All the substituted cyclohexenes exhibit maxima in the region of 260 to 280 nm while the cyclopentenenes and cyclohexenes do not. This may prove of use for identification purposes if it is not due to an impurity or to oxygen.

The possibility that the transitions were from aromatic impurities was remote, since the diolefins were never in contact with any aromatic solvents or compounds. This resemblance must be superficial.

Other Physical Methods of Monomer Analysis

It has been proposed by Butler [1, 7] that the nonconjugated interactions might be a ground state phenomena. It would therefore seem logical to also investigate the monomers with a ground state instrument. Two such available methods are NMR and IR spectroscopy.

The allyl-substituted cyclopentenes and cyclohexenes all produced spectra in which there was extensive spin-spin coupling and hence much splitting of the absorption peaks. Because of this splitting, the assignment of  $\delta$  values to specific protons was very difficult and uncertain. It was decided that further investigations into these diolefins would have to be done with spin decoupling equipment which was not available at the time.

The NMR spectrum of 1,4-dimethylenecyclohexane was determined, and the results were compared with those reported for certain methylenecycloalkanes [51]. The following absorptions were obtained for the methyleneprotons: 1,4-dimethylenecyclohexane, 4.63  $\delta$ ; methylenecyclohexane, 4.55  $\delta$ ; methylenecyclopentane, 4.82  $\delta$ ; and methylenecyclobutane, 4.70  $\delta$ .

Conjugated terminal methylene groups generally absorb at 4.90  $\delta$  while unconjugated methylenes absorb at 4.65  $\delta$  [52]. Since 1,4-dimethylenecyclohexane appeared to fall in the unconjugated region and the model exocyclic olefins behaved inconsistently, the investigation was not pursued further.

Infrared spectroscopy should be a suitable method for investigations of ground state interactions. A relationship exists between the force constant of the bond and its absorption frequency. Factors which affect the strength of the bonding would then be expected to also affect the IR absorption frequency of that bond.

There is some evidence that the force constant is related to the mobile bond order ( $p$ ) obtained from molecular orbital calculation. Work of Longuet-Higgins and Burkett on conjugated acetylenes supports this relationship [53].

If there is an interaction between nonconjugated diolefins, it might be possible to detect the interaction by a decrease in the frequency of the carbon-carbon stretching frequency. As the carbon-carbon double bonds interact with each other, there should be more single bond character to the double bond, hence shifting the absorption to lower energies. In the usual example of ethylene and butadiene, the stretching frequency is shifted from 1623  $\text{cm}^{-1}$  (Raman) in ethylene to 1597  $\text{cm}^{-1}$  in butadiene.

Table 10 lists the stretching frequencies obtained on the monomers studied in this dissertation. There is clearly very little variance between the diolefins and the corresponding monolefins. Such small differences as are found in the table have no meaning since the accuracy of the IR instrument used was just 4  $\text{cm}^{-1}$ .

TABLE 10. Infrared Absorption Values of Some Unsaturated Hydrocarbons

Compound	Frequency (cm <sup>-1</sup> )		
	HC=CH	C=CH <sub>2</sub>	CH <sub>2</sub> wag
Methylenecyclohexane	-	1651	887
Dimethylenecyclohexane	-	1655	890
Methylenecyclopentane	-	1660	872
3-Allylcyclohexene	1653	1642	912
4-Allylcyclohexene	1651	1643	910
4-Vinylcyclohexene	1652	1642	912
Allylcyclohexane	-	1642	910
3-Propylcyclohexene	1647	-	-
Cyclohexene	1650	-	-
3-Allylcyclopentene	1614	1642	910
4-Allylcyclopentene	1616	1644	912
Cyclopentene	1615	-	-
1,6-Heptadiene	-	1642	910
1-Hexene	-	1642	910

It can be concluded that there is no evidence for interaction in these systems. Either the interaction is nonexistent or it is too small to be detected with the above precision. It may also be that the above reasoning is not applicable.

Potts and Nyquist [ 54 ] have investigated the out-of-plane deformation frequency of the terminal methylene group. This absorption band is often referred to as a "methylene wag" since both hydrogen atoms move out of plane in the same direction. The authors found that this absorption is very sensitive to resonance effects of the substituents bonded to the olefin.

Substituents which donate electrons by resonance, as in methyl vinyl ether, shift the absorption to lower frequencies. Electron-withdrawing groups, such as in acrylonitrile, shift the absorption in the opposite direction.

Table 10 also lists the experimental values for the wagging frequencies. Again, there is only a slight variation among the olefins. The

abnormal value for the methylenecyclopentane probably reflects the greater strain caused by the smaller ring.

In summary then, no evidence was found for support of a ground state interaction in the systems studied.

## EXPERIMENTAL

All temperatures are reported uncorrected in degrees centigrade. Ultraviolet spectra were obtained with a nitrogen purged Beckman Model DK-2A Ratio Recording Spectrophotometer equipped with far-UV silica optics and cells. Wavelengths were calibrated with mercury emission lines. Nuclear magnetic resonance spectra were obtained either on a Varian V-4302 High Resolution Nuclear Magnetic Resonance Spectrometer or on a Varian A-60A Analytical NMR Spectrometer. Infrared spectra were obtained either with a Perkin-Elmer Infracord Infrared Recording Spectrophotometer, a Perkin-Elmer Model 21 Infrared Recording Spectrophotometer, or a Beckman IR IO Infrared Spectrophotometer. Vapor phase chromatographic analyses (VPC) were carried out either on a FM Model 700 Laboratory Chromatograph or on a Wilkens Aerograph Hi Fy Model 600-D Gas Chromatograph using helium as the effluent gas and a hydrogen flame detector. Refractive indices were obtained with a Bausch and Lomb Abbe 34 Refractometer equipped with an achromatic compensating prism. Melting point determinations were performed in open capillary tubes in a Thomas-Hoover Melting Point Apparatus. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

All common solvents and reagents were reagent grade products obtained from Fisher Scientific Co.; J. T. Baker Chemical Co.; Matheson, Coleman and Bell; or Eastman Organic Chemicals. 1,4-Cyclohexanedimethanol was obtained from Eastman Organic Chemicals and used as received. Methylenecyclohexane, methylenecyclopentane, and 1,6-heptadiene were obtained from the Columbia Organic Chemicals Co. 1-Hexene was obtained from Matheson, Coleman and Bell. 4-Vinylcyclohexene was obtained from KK Laboratories. Cyclohexene was obtained from Eastman Organic Chemicals. All olefins were distilled under  $N_2$  from  $CaH_2$  through a 23 plate spinning band column before use. 1,4-Cyclohexanediol was obtained from KK Laboratories and used as received. The spectrograde solvents used in the spectra were supplied as follows: isooctane (Fisher Scientific Co.), heptane (Fisher Scientific Co.), acetonitrile (Eastman Organic Chemicals and Columbia Organic Chemical Co.), and 95% ethanol (Union Carbide) (Table 11).

TABLE 11. Absorbance<sup>a</sup> of Solvents Used in the Far UV

Wavelength, nm	n- heptane	Iso- octane	Aceto- nitrile	95% Ethanol
200	.13	.08	.07	.11
197.5	.16	.08	.08	.13
195	.22	.09	.08	.16
192.5	.28	.09	.08	.15
190	.32	.10	.10	.40
187.5	.35	.10	.12	.78
185	.38	.10	.15	-
182.5	.38	.11	.24	-
180	.38	.19	.46	-
177.5	.37	.87	.90	-
175	.38	-	-	-
172.5	.48	-	-	-

<sup>a</sup>Solvent in sample cell vs nitrogen; 0.01 cm. Values are percent absorbance.

### Procedures for UV Spectroscopy

#### Nitrogen Purge

A nitrogen purge of 1.5 ft<sup>3</sup>/min was used below 190 nm and a purge of 0.3 ft<sup>3</sup>/min was used between 190 and 210 nm.

#### Concentration and Pathlengths for Solution Spectra

Below 210 nm, concentrations between 10<sup>-2</sup> M were used with the 0.01-cm far-UV cells. Above 210 nm, a concentration of 10<sup>-1</sup> M was used with 1 cm cells.

### Syntheses Related to Monomer Preparations

#### 1,4-Cyclohexanedimethyl Iodide

This compound was prepared according to the procedure of Ball [26]. Yield: 141.6 g (79%), mp 78 to 79°C.

### 1,4-Dimethylenecyclohexane

This compound was also prepared according to the procedure of Ball [26]. Yield: 6.03 g (45%), bp 60 to 60.5°C/98 Torr,  $n_D^{19.5}$

1.4734. Vapor phase chromatographic analysis over a dinonylphthalate column showed the presence of only one substance. Infrared analysis revealed the following absorption bands: 3080 and 2990  $\text{cm}^{-1}$  ( $\text{CH}_2=$ ), 1790  $\text{cm}^{-1}$  ( $\text{CH}_2$  out-of-plane overtone), 1655  $\text{cm}^{-1}$  (C=C stretching) and 890  $\text{cm}^{-1}$  (CH out-of-plane). Ultraviolet absorption spectroscopy yielded the following data: isooctane, 198.2 nm (21,110), shoulder 202.8 nm (18,514), shoulder 208.6 nm (10,287); 95% ethanol, 198.6 nm (19,454), shoulder 203.3 nm (17,201), shoulder 208.9 nm (9,554).

### 3-Chlorocyclopentene

This compound was prepared according to the procedure of Noller and Adams [55]. Yield: 78.7 g (69%), bp 25 to 30°C/26 Torr.

### 3-Allylcyclopentene

Allylmagnesium chloride was prepared according to the procedure of Kharasch and Reinmuth [32]. A 1-liter, three-necked flask was fitted with a mechanical stirrer, reflux condenser, addition funnel, and nitrogen inlet/bubbler. The apparatus was flamed out twice under nitrogen, cooled to room temperature, and charged with 78.7 g (0.79 mole) of 3-chlorocyclopentene in 100 ml of anhydrous ether and then wrapped with a towel containing Dry Ice. The allyl Grignard solution previously prepared from 1.0 mole of allyl chloride was cooled in an ice bath. The unsaturated halide was added slowly over 2 hr to the stirred Grignard solution and then the mixture was stirred at room temperature for 24 hr. The mixture was then carefully poured into a beaker of ice and acidified with a saturated solution of  $(\text{NH}_4)_2\text{SO}_4$  until clear. The two phases were then filtered free of unreacted magnesium metal, the ether layer separated, and the aqueous layer extracted four times (100 ml each) with ether. The ether layers were combined and dried over  $\text{MgSO}_4$ . Distillation through a 1.5 × 12 cm Vigreux column yielded 38.1 g (45.8% of colorless liquid, bp 81°C/481 Torr to 99°C/386 Torr,  $n_D^{20.5}$

1.4514. Distillation through a spinning band column (23 theoretical plates) yielded pure 3-allylcyclopentene, bp 95.5°C/348 Torr,  $n_D^{25.5}$  1.4530,  $D_4^{20}$  0.8039 g/ml. Vapor phase chromatographic analysis over a diisodecylphthalate column showed the presence of only one substance. Nuclear magnetic resonance spectroscopy confirmed the assigned structure with absorptions at 5.64  $\delta$  (=CH), 4.90  $\delta$  (=CH<sub>2</sub>), and 2.12  $\delta$  (CH,CH<sub>2</sub>). Infrared analysis revealed the following absorption bands: 3095, 3070, 3015, and 2995  $\text{cm}^{-1}$

(=CH and =CH<sub>2</sub>)<sub>2</sub>, 1835 cm<sup>-1</sup> (medium, =CH<sub>2</sub> out-of-plane overtone), 1650 and 1625 cm<sup>-1</sup> (C=C), 995 and 915 cm<sup>-1</sup> (-CH=CH<sub>2</sub>), and 720 cm<sup>-1</sup> (cis CH=CH). Other physical data: UV spectroscopy, 182.3 nm (17,367), n-heptane; 182.7 nm (15,416), acetonitrile. Near IR spectroscopy, 1.623 and 2.110 μ (-CH=CH<sub>2</sub>) and 2.136 μ (cis CH=CH).

Analysis: Calculated for C<sub>8</sub>H<sub>12</sub>: C, 88.82; H, 11.18. Found: C, 89.05; H, 11.06.

#### 4-Bromocyclopentene

This compound was prepared according to the procedure of Bartlett and Rice [29]. Yield: 20.5 g (10.5%), bp 58.5°C/47 Torr, n<sub>D</sub><sup>21</sup>

1.5016. Infrared analysis revealed the following absorption bands: 3095 cm<sup>-1</sup> (=CH), 1610 cm<sup>-1</sup> (C=C, very weak), and 735 cm<sup>-1</sup> (cis CH out-of-plane deformation).

#### 4-Allylcyclopentene

A 250-ml three-necked flask was fitted with a mechanical stirrer, reflux condenser, pressure equalizing addition funnel, and a nitrogen inlet/bubbler. The apparatus was flamed out twice under nitrogen, cooled, and then charged with 5.57 g (0.229 mole) of ether-washed magnesium metal, 60 ml of anhydrous ether, and a crystal of iodine. The addition funnel was loaded with 33.57 g (0.229 mole) of 4-bromocyclopentene in 50 ml of anhydrous ether. A small amount of the halide was added to the magnesium metal and then stirred until the reaction commenced. The additional halide was added over 2 hr at a rate to maintain a gentle reflux. The reaction was then refluxed 2 hr and cooled to room temperature.

A 500-ml, three-necked flask was fitted with a mechanical stirrer, reflux condenser, pressure equalizing addition funnel, and CaSO<sub>4</sub> drying tubes after having been flamed out twice under nitrogen. The mechanical stirrer of the flask containing the Grignard reagent was replaced by a tube containing a glass wool plug. The Grignard solution was forced through the plug into the 500-ml flask by means of nitrogen pressure. The unreacted magnesium was washed twice with 20 ml portions of anhydrous ether. The Grignard solution was cooled in an ice bath while the addition funnel was charged with 27.3 g (0.229 mole) of freshly distilled allyl bromide in 200 ml of anhydrous ether. The allyl bromide solution was added slowly to the Grignard solution over 2 hr with stirring. The solution was allowed to warm to room temperature while stirring overnight. The reaction product was a light yellow solution with a large amount of red-brown oil at the bottom of the flask. The mixture was poured slowly onto a beaker of ice and treated with a saturated solution of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> until clear. The ether layer was separated and the aqueous layer extracted three times (200, 100, 100 ml) with ether. The combined ether fractions were dried over MgSO<sub>4</sub> and then distilled through a

1.5 × 12 cm Vigreux column. Yield: 12.9 g of colorless liquid, bp 105 to 123°C. The distillate was carefully fractionated through a spinning band column (23 theoretical plates) to yield 10.1 g (40.9%) of 4-allylcyclopentene, bp 121 to 122°C/760 Torr,  $n_D^{21}$  1.4511,  $d_4^{20}$

0.8141 g/ml. Infrared analysis revealed the following absorption bands: 3090, 3070, 3010, and 2985  $\text{cm}^{-1}$  (=CH and =CH<sub>2</sub>), 1835  $\text{cm}^{-1}$  (weak, =CH<sub>2</sub> out-of-plane overtone), 1650 and 1620  $\text{cm}^{-1}$  (C=C, strong and medium), 992 and 912  $\text{cm}^{-1}$  (-CH=CH<sub>2</sub>), and 670  $\text{cm}^{-1}$  (cis C=C out-of-plane deformation). Nuclear magnetic resonance spectroscopy confirmed the structure. Vapor phase chromatography over diisodecylphthalate and 3,3'-oxydipropionitrile columns showed only one substance to be present. Other physical data: ultraviolet spectroscopy, 180.0 nm (18,621), n-heptane; 180.6 nm (19,340), acetonitrile. Near-IR spectroscopy, 1632 and 2.115  $\mu$  (-CH=CH<sub>2</sub>) and 2.137  $\mu$  (cis CH=CH).

Analysis: Calculated for C<sub>8</sub>H<sub>12</sub>: C, 88.82; H, 11.18. Found: C, 88.95; H, 11.36.

### 3-Bromocyclohexene

This compound was prepared according to the procedure of Bailey and Nicholas [56]. Yield: 39.53 g (56.2%), bp 60 to 62°C/15 Torr,  $n_D^{20}$  1.5308. Infrared analysis yielded the following absorption bands: 3090  $\text{cm}^{-1}$  (=CH), 1645  $\text{cm}^{-1}$  (C=C), and 730  $\text{cm}^{-1}$  (cis CH=CH).

### 3-Allylcyclohexene

Allylmagnesium chloride was prepared according to the procedure used in the preparation of 3-allylcyclopentene.

The addition funnel was loaded with 37.5 g (0.233 mole) of 3-bromocyclohexene in 200 ml of anhydrous ether. The unsaturated bromide was added to the allylmagnesium chloride solution at a rate to maintain a gentle reflux. Time of addition was 70 min. The reaction mixture was then stirred overnight at room temperature. The resulting white slurry was poured slowly into a beaker of ice and acidified with a saturated solution of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> until clear. The ether layer was separated and the aqueous layer extracted three times (100, 50, 50 ml) with ether. The combined ether extracts were dried over MgSO<sub>4</sub> and then distilled through a 1.5 × 12 cm. Vigreux distillation column. Yield: 17.91 g (71.5%), bp 88°C/89 Torr,  $n_D^{20}$  1.4682,  $d_4^{20}$  0.8264 g/ml. Vapor phase chromatographic analysis over a diisodecylphthalate column showed the presence of only one compound. Nuclear magnetic resonance spectroscopy confirmed the assigned structure with absorptions at 5.56  $\delta$  (=CH), 4.92  $\delta$  (-CH<sub>2</sub>), and 1.85  $\delta$  (CH, CH<sub>2</sub>). Infrared analysis revealed the following absorption bands: 3090, 3080, 3030, and 2995  $\text{cm}^{-1}$  (=CH and =CH<sub>2</sub>); 1835  $\text{cm}^{-1}$  (weak, =CH<sub>2</sub> out-of-plane overtone); 1650 and 1660  $\text{cm}^{-1}$  (C=C); 995 and 915  $\text{cm}^{-1}$  (-CH=CH<sub>2</sub>); and 725 and 685  $\text{cm}^{-1}$  (cis, CH=CH).



Other physical data: UV spectroscopy, 181.8 nm (18,841), n-heptane; 183.0 nm (17,614), acetonitrile. Near-IR spectroscopy, 1.620 and 2.110  $\mu$  ( $-\text{CH}=\text{CH}_2$ ) and 2.135  $\mu$  (cis  $\text{CH}=\text{CH}$ ).

Analysis: Calculated for  $\text{C}_9\text{H}_{14}$ : C, 88.45; H, 11.55. Found: C, 88.49; H, 11.46.

#### 4-Chlorocyclohexanol

This compound was prepared according to the procedure of Owens and Robins [57]. Yield: 72.2 g (62%) bp 70°C/6 Torr to 78°C/3 Torr,  $n_{\text{D}}^{19}$  1.4937. Infrared analysis revealed the following

absorption bands: 3400  $\text{cm}^{-1}$  ( $-\text{OH}$ ), 1065  $\text{cm}^{-1}$  (OH), and 745  $\text{cm}^{-1}$  (C-Cl).

#### 4-Chlorocyclohexene

This compound was prepared according to the procedure of Birch and Hunter [58]. Yield: 40.92 g (66%), bp 81.5 to 82°C/115 Torr,  $n_{\text{D}}^{20}$  1.4825. Vapor phase chromatographic analysis over a Carbowax 20M column showed the compound to be 99% pure. Infrared analysis revealed the following absorption bands: 3095  $\text{cm}^{-1}$  ( $=\text{CH}$ ), 1650  $\text{cm}^{-1}$  (C=C), and 675  $\text{cm}^{-1}$  (cis,  $\text{CH}=\text{CH}$ ).

#### 4-Allylcyclohexene

A 500-ml., three-necked flask was equipped with a mechanical stirrer, pressure equalizing addition funnel, reflux condenser, and a nitrogen inlet/bubbler. The apparatus was flamed out twice under nitrogen, cooled to room temperature, and then loaded with 8.8 g (0.36 mole) of ether-washed magnesium metal, a crystal of iodine, and 100 ml of anhydrous ethyl ether. Into the addition funnel was placed 38.5 g (0.33 mole) of redistilled 4-chlorocyclohexene in 100 ml of anhydrous ether. A small amount of the halide was added to the magnesium metal and then the mixture was vigorously refluxed for 40 min before the reaction began. The remaining halide was added over 1.5 hr while the reaction was cooled in ice.

A 1-liter, three-necked flask was equipped with a mechanical stirrer, pressure equalizing addition funnel, reflux condenser, and drying tubes after flaming out the apparatus under nitrogen. The Grignard solution was filtered into the 1-liter flask exactly as described in the preparation of 4-allylcyclopentene. To the ice-cooled Grignard solution was added 40.3 g (0.331 mole) of freshly distilled allyl bromide (bp 70°C) in 200 ml of anhydrous ether. The time of addition was 1.5 hr. An additional 100 ml of ether was added to the yellow-green solution since the precipitated white salts were too thick to allow easy stirring. The slurry was stirred overnight at room temperature, refluxed 1 hr, and then poured into a beaker of ice after cooling. Saturated  $(\text{NH}_4)_2\text{SO}_4$  was used to clarify the solution.

The ether layer was separated and the remaining aqueous layer was extracted three times (200, 100, 100 ml) with ether and dried over  $\text{MgSO}_4$ . Distillation through a  $1.5 \times 12$  cm Vigreux column yielded 24.21 g (59.9%) of colorless liquid, bp 89 to  $95^\circ\text{C}$  (130 Torr). This material was carefully fractionated through a 23-plate spinning band column to yield pure 4-allylcyclohexene, bp  $97^\circ\text{C}$  (132 Torr),  $n_D^{20.5}$

1.4658,  $d_4^{20.5}$  0.8320. Nuclear magnetic resonance supported the structure with absorptions at 5.58  $\delta$  ( $\text{CH}=\text{}$ ); 5.05 and 4.82  $\delta$  ( $\text{CH}_2=\text{}$ ); and 1.97, 1.66, and 1.50  $\delta$  ( $\text{CH}, \text{CH}_2$ ). Vapor phase chromatographic analysis over a diisodecylphthalate column showed the presence of only one material. Infrared analysis revealed the following absorption bands: 3080, 3385, and  $2085\text{ cm}^{-1}$  ( $\text{CH}=\text{}$  and  $\text{CH}_2=\text{}$ ),  $1830\text{ cm}^{-1}$  ( $\text{CH}_2=\text{CH}$  out-of-plane overtone); 1655 and  $1645\text{ cm}^{-1}$  ( $\text{C}=\text{C}$  stretch);  $990\text{ cm}^{-1}$  ( $\text{CH}$  out-of-plane, vinyl); and  $650\text{ cm}^{-1}$  ( $\text{CH}$  out-of-plane, cis). Near-IR analysis revealed vinyl absorptions at 1.630 and 2.117  $\mu$  and cis  $\text{CH}=\text{CH}$  absorption at 2.138  $\mu$ . Ultraviolet analysis revealed the following absorptions: 179.1 nm (21,545), n-heptane; 179.8 nm (19,471), acetonitrile.

Analysis: Calculated for  $\text{C}_9\text{H}_{14}$ : C, 88.45; H, 11.55. Found: C, 88.32; H, 11.61.

### Allylcyclohexane

This compound was prepared using the general procedure of Resseguier [33]. Yield: 57.0 g (92%) bp  $94^\circ\text{C}/129$  Torr,  $n_D^{20}$

1.4505. Nuclear magnetic resonance supported the structure with absorptions centering at 5.75, 4.90, and 1.5  $\delta$ . The ratio of  $\text{sp}^2$  to  $\text{sp}^3$  hydrogens experimentally found (1:12.98) was in excellent agreement with theory (1:13). Vapor phase chromatographic analysis over a diisodecylphthalate column revealed the presence of only one material. Infrared analysis revealed the following absorption bands: 3084 and  $2981\text{ cm}^{-1}$  ( $=\text{CH}_2$ ,  $=\text{CH}$  stretch),  $1842\text{ cm}^{-1}$  (overtone of out-of-plane deformation),  $1642\text{ cm}^{-1}$  ( $\text{C}=\text{C}$ ), and 993 and  $910\text{ cm}^{-1}$  (vinyl out-of-plane deformation). Ultraviolet analysis revealed the following absorptions: 180.5 nm (11,500), n-heptane; 181.1 nm (10,500), acetonitrile.

Analysis: Calculated for  $\text{C}_9\text{H}_{16}$ : C, 87.02; H, 12.98. Found: C, 87.08; H, 12.99.

### 3-Propylcyclohexene

This compound was prepared according to the procedure of Berlande [34]. Yield: 27.4 g (56.6%), bp 157.5 to  $158^\circ\text{C}$ ,  $n_D^{20}$

1.4680. Infrared analysis revealed the following absorption bands:  $3020\text{ cm}^{-1}$  ( $=\text{CH}$  stretch),  $1647\text{ cm}^{-1}$  ( $\text{C}=\text{C}$  stretch), 710 and  $665\text{ cm}^{-1}$  (cis,  $\text{CH}=\text{CH}$  out-of-plane deformation) and  $735\text{ cm}^{-1}$  (propyl).

Nuclear magnetic resonance spectra supported the structure with an absorption centered at 5.65  $\delta$ , a quartet centered at 1.07  $\delta$ , and a triplet centered at 0.66  $\delta$ . The ratio of  $sp^2$  to  $sp^3$  hydrogens experimentally found (1:7.09) was in good agreement with theory (1:7). Ultraviolet analysis revealed the following absorptions: 186.1 nm (9,3000), n-heptane; 186.4 nm (8700), acetonitrile.

Analysis: Calculated for  $C_9H_{16}$ : C, 87.02; H, 12.98. Found: C, 86.88; H, 13.05.

#### ACKNOWLEDGMENTS

One of us (J.J.V.H.) was the recipient of both the Texaco Fellowship and the Armstrong Fellowship during the course of this work for which we are grateful.

#### REFERENCES

- [1] G. B. Butler, *J. Polym. Sci.*, **48**, 227 (1960).
- [2] C. S. Marvel, *Ibid.*, **48**, 101 (1960).
- [3] G. B. Butler, *Encyclopedia of Polymer Science and Technology*, Vol. 4, Wiley-Interscience, New York, 1966, p. 588.
- [4] S. G. Matsoyan, *Russ. Chem. Rev. (Eng. Transl.)*, **35**, 32 (1966).
- [5] W. E. Gibbs and J. M. Barton, "Kinetics and Mechanisms of Polymerization," in *Vinyl Polymerization*, Vol. 1, Part 1 (G. E. Ham, ed.), Dekker, New York, 1967, p. 59.
- [6] G. B. Butler and M. A. Raymond, *J. Polym. Sci., A*, **3**, 3413 (1965).
- [7] G. B. Butler, Paper presented before International Symposium on Macromolecular Chemistry, Moscow, U.S.S.R., June, 1960: *Papers and Summaries, Section I*, pp. 74-78.
- [8] C. S. Marvel and J. K. Stille, *J. Amer. Chem. Soc.*, **80**, 1740 (1958).
- [9] G. B. Butler and J. J. Van Heiningen, *J. Macromol. Sci.—Rev., Macromol. Chem.*, In Press.
- [10] N. D. Field, *J. Org. Chem.*, **25**, 1006 (1960).
- [11] R. T. Morrison and R. N. Boyd, *Organic Chemistry*, Allyn and Bacon, Boston, 1959, p. 184.
- [12] R. S. Silas, J. Yates, and V. Thornton, *Anal. Chem.*, **31**, 529 (1959).
- [13] G. B. Butler and S. Kimura, *J. Macromol. Sci.—Chem.*, **A5**(1), 181 (1971).
- [14] D. J. Carlsson and K. U. Ingold, *J. Amer. Chem. Soc.*, **90**, 704T (1968).
- [15] G. B. Butler and T. W. Brooks, *J. Org. Chem.*, **28**, 2699 (1963).

- [16] H. H. Jaffe and M. Orchin, Theory and Applications of Ultra-violet Spectroscopy, Wiley, New York, 1962, p. 437.
- [17] G. B. Butler and M. A. Raymond, J. Org. Chem., **30**, 2410 (1965).
- [18] C. S. Marvel and C. C. L. Hwa, J. Polym. Sci., **45**, 25 (1960).
- [19] G. B. Butler and M. A. Raymond, J. Macromol. Chem., **1**, 201 (1966).
- [20] E. A. Braude, Ann. Rep., **42**, 105 (1945).
- [21] C. S. Marvel and J. K. Stille, J. Amer. Chem. Soc., **80**, 1740 (1958).
- [22] P. D. Bartlett and S. Bank, Ibid., **83**, 2591 (1961).
- [23] W. D. Clossen and G. T. Kwiatkowski, Ibid., **86**, 1887 (1964).
- [24] S. Winstein and P. Carter, Ibid., **83**, 1485 (1961).
- [25] P. D. Bartlett et al., Ibid., **87**, 1288 (1965).
- [26] L. E. Ball, Ph.D. Dissertation, University of Akron, 1960.
- [27] G. Wittig and V. Schoellkopf, Org. Syn., **40**, 66 (1960).
- [28] E. J. Corey et al., J. Org. Chem., **28**, 1128 (1963).
- [29] P. D. Bartlett and M. R. Rice, Ibid., **28**, 3351 (1963).
- [30] C. R. Johnson and J. E. Keiser, Tetrahedron Lett., **45**, 3827 (1964).
- [31] P. D. Bartlett and G. D. Sargeant, J. Amer. Chem. Soc., **87**, 1297 (1965).
- [32] M. S. Kharasch and O. Reinmuth, J. Org. Chem., **9**, 359 (1944).
- [33] M. B. de Resseguier, Bull. Soc. Chim. Fr., **7**, 432 (1910).
- [34] A. Berlande, Chem. Abstr., **38**, 722 (1944).
- [35] H. Ley and H. Dirking, Chem. Ber., **67**, 1331 (1934).
- [36] A. Streitwieser, Jr., Molecular Orbital Theory for Organic Chemists, Wiley, New York, 1962, p. 207.
- [37] W. Kaye, Symposium on Spectroscopy, Special Technical Publications, No. 269, American Society for Testing and Materials, Philadelphia, 1959, p. 63.
- [38] J. D. Roberts, Notes on Molecular Orbital Calculations, Benjamin, New York, 1962, p. 82.
- [39] H. J. Kopineck, Z. Naturforsch., **5A**, 420 (1950).
- [40] R. F. Orloski, Ph.D. Dissertation, University of California, Los Angeles, 1963.
- [41] W. C. Price et al., Spectrochim. Acta, **14**, 45 (1959).
- [42] R. Filler et al., J. Chem. Eng. Data, **9**, 370 (1964).
- [43] W. C. Price et al., Proc. Roy. Soc., A, 258, 459 (1960).
- [44] N. C. Brown et al., in Determination of Organic Structures by Physical Methods (E. A. Braude and F. C. Nachod, ed.), Academic, New York, 1955, p. 567.
- [45] P. D. Bartlett et al., J. Amer. Chem. Soc., **87**, 1314 (1965).
- [46] C. P. Snow and C. B. Allsopp, Trans. Faraday Soc., **30**, 93 (1934).
- [47] C. Reid, J. Chem. Phys., **18**, 1299 (1950).
- [48] D. F. Evans, J. Chem. Soc., 1960, 1735.

- [49] R. S. Berry, J. Chem. Phys., **38**, 1934 (1963).
- [50] W. J. Potts, Jr., Ibid., **23**, 65 (1955).
- [51] NMR Spectra Catalogue, Vol. 1, Varian Associates, 1962.
- [52] L. M. Jackman, Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, Pergamon, New York, 1959, p. 61.
- [53] H. C. Longuet-Higgins and F. H. Burkett, Trans. Faraday Soc., **48**, 1077 (1952).
- [54] W. J. Potts and R. A. Nyquist, Spectrochim. Acta, **15**, 679 (1959).
- [55] C. R. Noller and R. Adams, J. Amer. Chem. Soc., **48**, 2444 (1926).
- [56] W. J. Bailey and L. Nicholas, Ibid., **21**, 854 (1956).
- [57] L. N. Owens and P. A. Robins, J. Chem. Soc., 1949, 320.
- [58] S. F. Birch et al., J. Org. Chem., **23**, 1026 (1958).

Accepted by editor March 28, 1974

Received for publication April 10, 1974