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### The Fundamental Basis for Cyclopolymerization. VIII. An Ultraviolet Spectral Study of Certain Unsymmetrical 1,6-Heptadienes

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## The Fundamental Basis for Cyclopolymerization. VIII. An Ultraviolet Spectral Study of Certain Unsymmetrical 1,6-Heptadienes\*

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### ABSTRACT

In an effort to study unsymmetrical 1,6-heptadienes which may form intramolecular charge-transfer complexes and thus enhance their cyclopolymerization characteristics via free-radical initiation, 2-phenylallyl methacrylate, 2-phenylallyl-2'-carboethoxyallyl ether, methallyl methacrylate, 2-phenylallyl ether, 2-phenylallyl methallyl ether, and all of the corresponding monoenes were prepared. The dienes and their corresponding monoenes were studied by IR, NMR, and UV spectroscopy in an attempt to detect a possible ground state electronic interaction in the dienes. No ground state electronic interaction was observed.

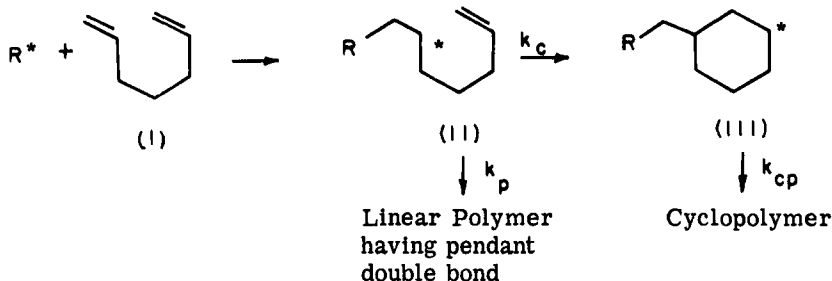
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\*Presented in part before the Division of Polymer Chemistry, American Chemical Society, Houston, Texas, February 1970; taken from the Ph.D. Dissertation of Keith B. Baucom, University of Florida, 1971; for Paper VII of this series, see *J. Macromol. Sci.—Chem.*, **A8(7)**, 1175 (1974).

1205

## INTRODUCTION

Cyclopolymerization of nonconjugated dienes to soluble, gel-free polymers is well established and accepted, but the mechanism leading to cyclic polymer units has not been established. A number of reviews [1-5] discussing cyclopolymerization are available. The most probable steps involved in the cyclopolymerization of a 1,6-heptadiene are where  $R^*$  is a cation, free radical, or anion.



The reaction of the initiator with the 1,6-heptadiene (I) gives the Intermediate II which may react intermolecularly to form a linear polymer having pendant double bonds or intramolecularly to form cyclopolymer. Polymerization to polymers having pendant double bonds eventually leads to cross-linked polymer. The cyclization step, being unimolecular, is independent of monomer concentration while the rate of linear propagation increases with monomer concentration. The ratio of the cyclization rate constant  $k_c$  to the linear propagation rate constant  $k_p$  combined with the monomer concentration is an indicator of the cyclic nature of the polymer. The value of  $k_c/k_p$  generally ranges from 5 to 20 moles/liter [5]. Butler and Kimura [6] have reported from kinetic studies the intramolecular double bond concentration with respect to the neighboring radical in cyclopolymerization of 2,6-dicyano-1,6-heptadiene to be  $\geq 20.4$  moles/liter, a physically impossible situation, since the concentration of liquid ethylene at its boiling point,  $-102^\circ\text{C}$ , is only 21.8 moles/liter. Recent studies on radical cyclizations by Carlsson and Ingold [7] have indicated such hypothetical concentrations to go as high as 100 moles/liter.

Two mechanisms have been proposed in an attempt to explain why cyclization is favored over intermolecular propagation to the extent that many nonconjugated dienes give nearly totally cyclized polymer. One argument emphasizes electronic effects while the other is based mainly on steric arguments.

Butler [8] proposed that the activation energy for the cyclization step might be lowered by an electronic interaction which could exist between the double bonds of the 1,6-diene.

The effect of an electronic interaction on polymerization would be to provide an energetically favored pathway for cyclization as opposed to polymerization resulting in pendant double bonds. Evidence supporting this proposed mechanism would have to show a direct correlation between the extent of the electronic interaction and the degree of cyclopolymerization.

Experimental evidence for electronic interaction of nonconjugated  $\pi$ -electron systems should be sought in the spectral and ionization properties of the systems [9]. In the past for nonconjugated systems, the absorption for multiple chromophoric species was expected to be the exact sum of the absorptions due to each component chromophore.

$$A_{\lambda abc \dots} = A_{\lambda a} + A_{\lambda b} + A_{\lambda c} \dots$$

Exceptions to this rule of additivity for nonconjugated chromophoric systems have been observed. A review entitled "Nonconjugated Chromophoric Interactions in the Ultraviolet" has been made by Butler and Van Heiningen [10]. These effects have been defined by Jaffe and Orchin [11] as those "which correspond neither to the simple addition of the spectra of the two insulated chromophores, nor to the spectra of the completely conjugated systems."

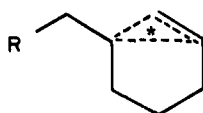
Butler and Raymond [12] synthesized a series of tetraenes which had two pairs of conjugated double bonds situated in such a manner that an electronic interaction might occur and compared their spectra with suitable model dienes. A bathochromic shift of 10.6 nm was observed when 1,3,6,8-nonatriene was compared with 1,3-nonadiene, while comparison of 1,3,9,11-dodecatetraene with 1,3-dodecadiene indicated a bathochromic shift of 2.7 nm. These data were interpreted as a strong indication that interactions occur.

Butler and Van Heiningen [13] compared the UV absorption spectrum of 1,4-dimethylenecyclohexane with that of methylenecyclohexane. A bathochromic shift in the absorption maxima and the appearance of two longer wavelength shoulders were observed. These results were discussed in terms of an electronic interaction.

Butler and Iachia [14] have provided some of the most significant evidence in support of nonconjugated electronic interaction in 1,6-dienes. The UV absorption spectra of allyltrimethylsilane, diallyldimethylsilane, triallylmethylsilane, and tetraallylsilane were compared. It was found that, as the number of allyl groups was increased, the absorption maxima were shifted to longer wavelength. In addition, the extinction coefficients were nonadditive. This was interpreted as strong evidence for nonconjugated electronic interaction.

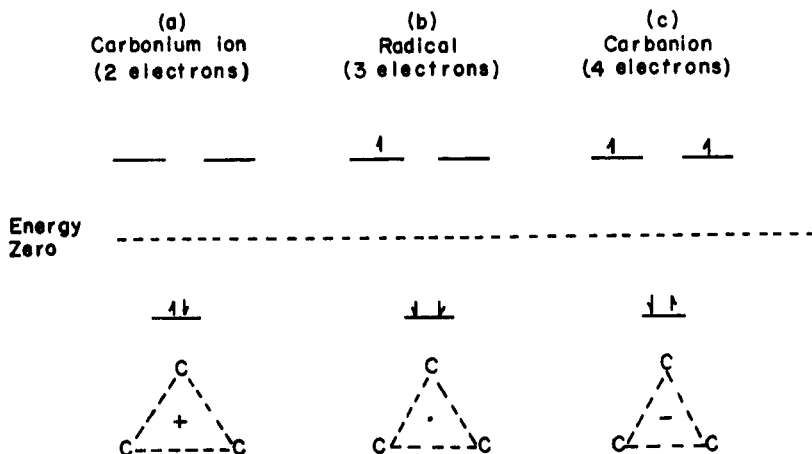
Although there is considerable evidence supporting nonconjugated electronic interactions in selected dienes, there has been no correlation made between the extent of an electronic interaction and the tendency of the diene to undergo cyclopolymerization.

Butler [15] and Marvel and Stille [16] have also suggested that an electronic interaction might exist between the pendant double bond and the radical [15] or ion [16] generated by the initiating species. Such structures may be represented by IV (\* = cation, anion, or radical).

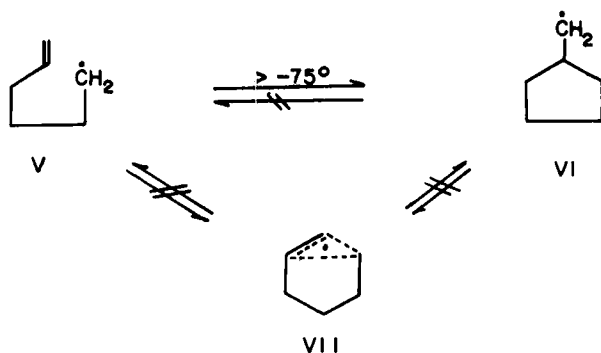


(IV)

The three orbitals for a three-atom structure such as IV consist of one bonding orbital and two degenerate antibonding orbitals [17]. Electrons in the antibonding orbitals destabilize the system and raise its energy. Simple molecular orbital calculations indicate that a tricentric transition state involving two or three electrons is favored when triangular; while with four electrons, a linear transition state is favored [17]. The carbonium ion a has been shown to have considerable stability. Ions of this type have been observed by NMR [18]. The

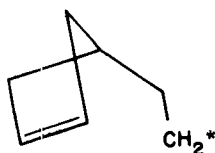


anion c has been referred to as antiaromatic [19, 20]. The radical b has not yet been observed. Kochi and Krusic [21] studied the ESR spectrum of 5-hexenyl radical at variable temperatures. At  $-78^{\circ}\text{C}$  the 5-hexenyl radical V was observed. At  $-35^{\circ}\text{C}$  only cyclopentylmethyl radical VI was detected. Both species were present at intermediate temperatures. The nonclassical radical VII was not observed.



Carlsson and Ingold [7] reported the cyclization rate constant for the above reaction to be  $1 \times 10^5 \text{ sec}^{-1}$ . James and Ogawa [22] reported on the addition of ethyl radicals to heptene-1 in the gas phase measured relative to the rate of ethyl radical combination. At  $40^\circ\text{C}$  their data give a value of  $1 \times 10^3 \text{ m}^{-1} \text{ sec}^{-1}$  for the rate constant for addition. In the words of Carlsson and Ingold [7], this gave an "effective" double bond concentration of 100 M for the intramolecular cyclization. No simple explanation is presently available for these observations.

Wilt, Massic, and Dabek [23] discuss the differences in ring closure of the  $\Delta^3$ -cyclopentenyl ethyl carbonium ion, radical, and anion VIII:



VIII

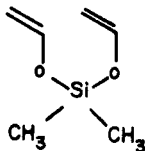
where \* = cation, radical, or anion.

Both the cation and radical undergo facile ring closure while the anion does not form cyclic product. These authors indicate that this may be viewed as an example of the fact that a tricentric transition state involving two or three electrons is favored when triangular; while with four electrons, a linear transition state is favored. In this example a linear arrangement of the three centers involved is sterically impossible.

It is again important to point out that proving the existence of IV is not evidence in itself that it exists on the reaction path leading to cyclopolymerization.

The work of Field [24] causes doubt as to the necessity of IV in bringing about cyclopolymerization. He polymerized 2,6-diphenyl-1,6-heptadiene by free radical, cationic, anionic, and Ziegler-type initiation to give in all cases soluble polymers of essentially the same structure with few or no double bonds detectable in the IR spectrum. The best method for obtaining both high conversion and high molecular weight was anionic polymerization. It has already been stated that structures such as IV, having four electrons, are not allowed. If structures such as IV were necessary in order for cyclopolymerization to occur, anionic polymerization would have resulted in polymer having pendant double bonds. It must be remembered that the anion, cation, or radical in this system is benzylic and therefore already well stabilized. This would decrease the tendency of formation of stabilizing structures such as IV during polymerization.

Nozakura and co-workers [25, 26] polymerized divinyloxydimethylsilane (IX) using both radical and cationic initiators. Radical polymerization gave polymers containing five-membered rings,



IX

six-membered rings, and pendant vinyl groups. Polymerization using cationic catalysts proceeded without cyclization in toluene or nitroethane and only a little cyclopolymerization occurred in methylene chloride. If structures such as IV were necessary for the occurrence of cyclopolymerization in this system, cationic initiation should have given a higher degree of cyclopolymerization than free radical initiation.

In summary, it may be said that there has been no evidence reported which shows that structures such as IV are necessary for the occurrence of cyclopolymerization.

Gibbs and Barton [5] have proposed that steric factors bring about cyclopolymerization. They note that a pendant group on the  $\beta$ -carbon of a monovinyl monomer has a significant effect on the absolute rate constants for propagation and termination. The  $k_p$  (30°C) and  $k_t$  (30°C) values for methyl acrylate and butyl acrylate are 720 vs 14 and  $2.2 \times 10^6$  vs  $9 \times 10^3$  liters/mole sec, respectively. The presence of the pendant group shields the radical. If the size of the pendant group is such that a conveniently sized cyclic structure can be formed by the

cyclization reaction, the double bond will frequently be presented to the radical on the  $\beta$ -carbon in a configuration favorable to reaction. The cyclized radical will have less steric hindrance than the uncyclized radical, thereby causing it to react faster.

Neither of the proposed mechanisms is able to account for all the major characteristics of cyclopolymerization. The lack of correlation between extent to which an interaction occurs and the degree to which cyclopolymerization occurs has been discussed. The basis of postulating that electronic interaction may take place and favor cyclization over intermolecular propagation is the belief that the formation of the pseudocyclic intermediates would lower the activation energy for the cyclization reaction. One major weakness of this proposed mechanism arises from the fact that there have been no cases reported where the activation energy for cyclization has been less than the activation energy for linear propagation,  $E_c < E_{11}$  [5]. In most cases  $E_c \geq E_{11}$ .

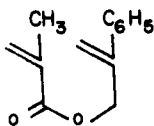
The steric-control mechanism suffers also from the fact that  $E_c - E_{11}$  experimentally is most often greater than zero and that the reactivity (overall rate of polymerization) of the diolefinic monomer is almost always greater than the reactivity of closely related monoenes [5].

The purpose of this research was to synthesize a series of dienes capable of cyclopolymerization and to determine their tendency to cyclize. The monomers and their corresponding monoenes were studied by spectral methods in an attempt to determine whether ground state electronic interactions could be detected. It is well known that an equimolar mixture of styrene and methyl methacrylate undergoes free-radical initiated copolymerization to yield a random copolymer containing approximately equimolar amounts of each monomer. On the other hand, cationic initiation of the same equimolar mixture of the monomer pair leads almost totally to the homopolymer of styrene while anionic initiation leads almost exclusively to the homopolymer of methyl methacrylate [27]. Although an original purpose of this research effort was to synthesize suitably substituted 1,6-heptadienes to permit a reasonable analogy to be drawn between these monomers and the styrene-methyl methacrylate monomer pair in the three types of initiation, synthetic difficulties in obtaining the necessary quantities of the diene monomers have precluded comparison of the extent of cyclization of these monomers for each initiating system. However, we would like to report the studies to date, which are predominantly free-radical initiated, on a series of diene monomers which were predicted on the basis of the analogous monoene systems to be capable of forming intramolecular charge-transfer complexes and thus cyclopolymerization would be predicted to be the predominant mode of radical initiated propagation. Although neither steric nor electronic factors can be duplicated exactly in analogies of this kind, it appeared reasonable that some information

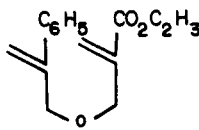


would be obtained which could be useful in further elucidation of the remaining uncertain aspects of an acceptable mechanism of cyclopolymerization.

Two of the dienes prepared were 2-phenylallyl methacrylate (XII) and 2-phenylallyl-2'-carboethoxyallyl ether (XVII). From an



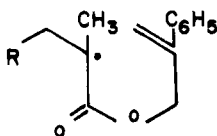
XII



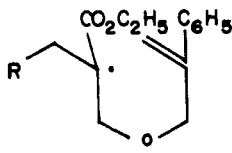
XVII

electronic standpoint there should be little difference in the two systems, but from a steric viewpoint there should be more strain in the transition state as the methacrylate radical attacks the 2-phenylallyl double bond [6]. A comparison was made in the relative tendency of the two systems to undergo cyclization. These results will be reported in the following paper.

The tendency of the two systems to undergo cyclization was also compared with the free radical copolymerization of methyl methacrylate with  $\alpha$ -methylstyrene. Methyl methacrylate radical tends to react with  $\alpha$ -methylstyrene twice as fast as it reacts with methyl methacrylate.  $\alpha$ -Methylstyrene radical tends to react with methyl methacrylate seven times as fast as it reacts with  $\alpha$ -methylstyrene [28]. This would indicate that there should be a high tendency for cyclization to occur in the two systems discussed above.



X



XI

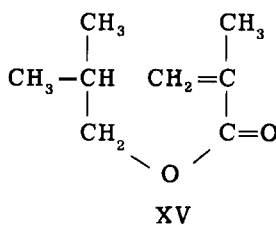
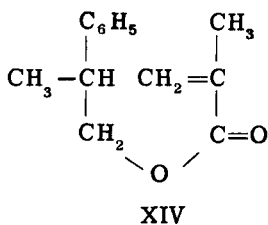
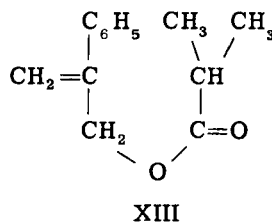
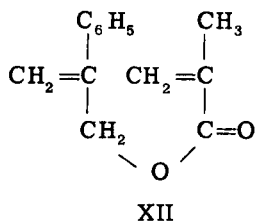
## RESULTS AND DISCUSSION

### Synthesis of Monomers

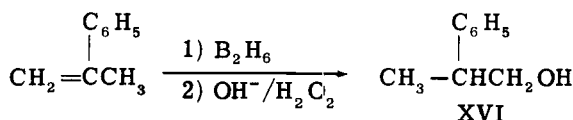
#### 2-Phenylallyl Methacrylate and Its Corresponding Monoenes

The first compounds chosen for study were 2-phenylallyl methacrylate (XII) and its corresponding monoenes, 2-phenylallyl isobutyrate (XIII),  $\beta$ -phenyl-n-propyl methacrylate (XIV), and isobutyl methacrylate (XV).

2-Phenylallyl methacrylate (XII) was prepared by the reaction of 2-phenylallyl alcohol with methacrylyl chloride. After this work had been completed, the synthesis of this compound was reported [29, 30]. 2-Phenylallyl isobutyrate (XIII) was prepared by the reaction of 2-phenylallyl alcohol with isobutyryl chloride.



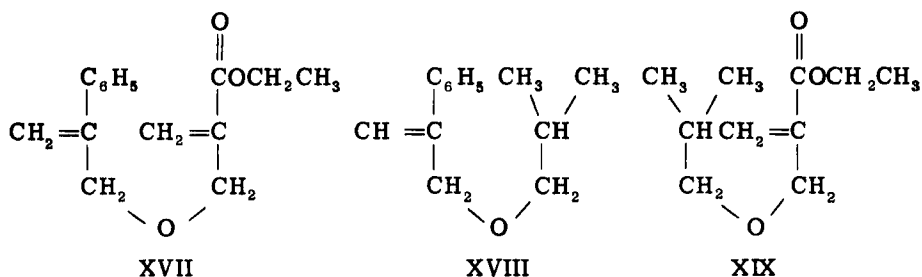
In order to prepare  $\beta$ -phenyl-*n*-propyl methacrylate (XIV), it was necessary to prepare  $\beta$ -phenyl-*n*-propyl alcohol (XVI). This was carried out according to the general procedure of Brown [31].  $\alpha$ -Methylstyrene was treated with diborane, and the product borane was hydrolyzed to the alcohol.



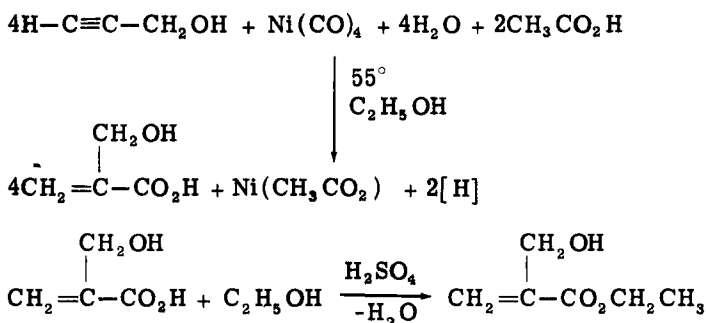
$\beta$ -Phenyl-*n*-propyl methacrylate was prepared from  $\beta$ -phenyl-*n*-propyl alcohol and methacrylyl chloride.

### 2-Phenylallyl-2'-carboethoxyallyl Ether and Its Corresponding Monoenes

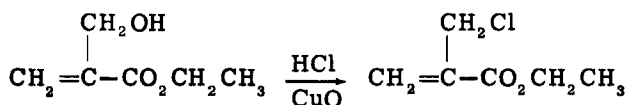
2-Phenylallyl-2'-carboethoxyallyl ether (XVII), 2-phenylallyl isobutyl ether (XVIII), and 2-carboethoxyallyl isobutyl ether (XIX) were also prepared for these studies.



In order to prepare 2-phenylallyl-2'-carboethoxy allyl ether, it was necessary to prepare ethyl- $\alpha$ -(hydroxymethyl)acrylate. This was carried out according to the procedure of Rosenthal, Schwartzman, Greco, and Proper [32].



The ethyl- $\alpha$ -(hydroxymethyl)acrylate was then converted to ethyl- $\alpha$ -(chloromethyl)acrylate according to the procedure of the Koppers Co. [33].



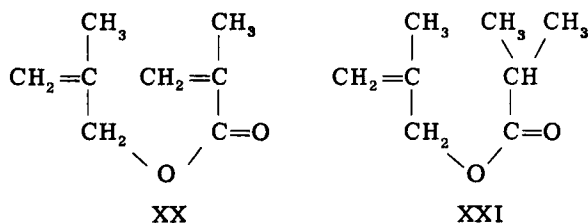
2-Phenylallyl-2'-carboethoxyallyl ether was then prepared by the addition of a dimethyl sulfoxide solution of sodium 2-phenylallyloxyde to ethyl- $\alpha$ -(chloromethyl)acrylate in dimethyl sulfoxide.

2-Phenylallyl isobutyl ether was prepared by the reaction of sodium isobutoxide with 2-phenylallyl chloride in dimethyl sulfoxide.

2-Carboethoxyallyl isobutyl ether was prepared by the reaction of sodium isobutoxide with ethyl- $\alpha$ -(chloromethyl)acrylate in dimethyl sulfoxide.

Methallyl Methacrylate and Its Corresponding Monoenes

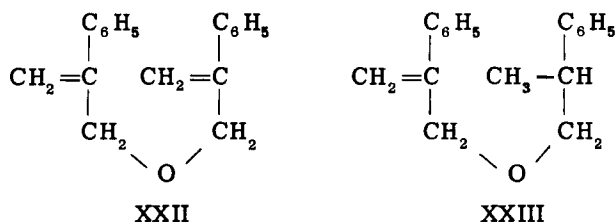
Methallyl methacrylate (XX) and its corresponding monoenes, isobutyl methacrylate (XVI) (reported previously) and methallyl isobutyrate (XXI), were also prepared for use in these studies.



Although all of these compounds are known, they were prepared in order to compare their spectral properties with those of 2-phenylallyl methacrylate and its corresponding monoenes. They were prepared from their respective alcohols and acid chlorides.

2-Phenylallyl Ether and Its Corresponding Monoenes

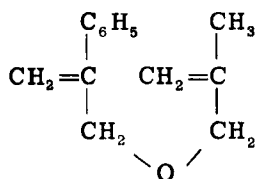
Also prepared for study were 2-phenylallyl ether (XXII) and its corresponding monoenes, 2-phenylallyl-2'-phenyl-n-propyl ether (XXIII) and 2-phenylallyl isobutyl ether (XVIII) (reported previously).



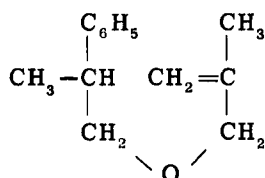
2-Phenylallyl ether was prepared from sodium 2-phenylallyloxyde and 2-phenylallyl chloride in dimethyl sulfoxide. 2-Phenylallyl-2'-phenyl-n-propylether was prepared from sodium 2-phenyl-n-propoxyde and 2-phenylallyl chloride in dimethyl sulfoxide.

2-Phenylallyl Methallyl Ether and Its Corresponding Monoenes

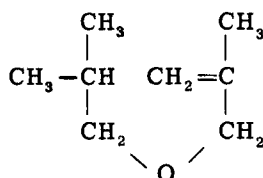
The next compounds chosen for study were 2-phenylallyl methallyl ether (XXIV) and its corresponding monoenes, 2-phenylallyl isobutyl ether (XVIII) (reported previously),  $\beta$ -phenyl-n-propyl methallyl ether (XXV), and isobutyl methallyl ether (XXVI).



XXIV



XXV



XXVI

2-Phenylallyl methallyl ether was prepared from sodium methallyl-oxide and 2-phenylallyl chloride in dimethyl sulfoxide.  $\beta$ -Phenyl-n-propyl methallyl ether was prepared from sodium  $\beta$ -phenyl-n-propoxide and methallyl chloride in dimethyl sulfoxide. Methallyl isobutyl ether was prepared from sodium isobutoxide and methallyl chloride in isobutyl alcohol.

The structure and purity of all compounds prepared were established by IR, NMR, and UV analysis, as well as elemental analysis when required, and gas-liquid chromatography (GLC) analysis.

### Infrared Spectra of Monomers

Infrared spectroscopy should be capable of detecting ground state electronic interactions between nonconjugated double bonds. Factors which affect the strength of a bond would affect the IR absorption frequency of that bond.

In the ground state electronic interaction theory previously proposed [8], new bond formation must occur at the expense of the existing double bonds. As the double bonds interact with each other, there should be more single bond character to these double bonds. This should cause a decrease in the carbon-carbon stretching frequency. In this 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 [10].

Table 1 lists the olefinic stretching frequencies obtained for the monomers studied in this work. There is little variation between the dienes and their corresponding monoenes. The precision with which

TABLE 1. Infrared Absorption Values for Monomers Studied

Compound	Frequency (cm <sup>-1</sup> )		
XVIII	1632	1601	1575
XXIII	1632	1603	1576
XXII	1632	1602	1576
XXIV	1660	1632	1602
XXVI	1660		1578
XXV	1660	1602	
XIII	1636	1603	1576
XIV	1640	1604	
XII	1640	1602	1577
XIX	1640		
XIV	1635	1600	1575

the frequencies are observed can be no better than 5 cm<sup>-1</sup>. From these data, there is no indication of an interaction.

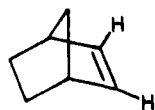
### NMR Spectra of Monomers

Nuclear magnetic resonance spectroscopy should be a valuable tool in detecting ground state electronic interactions of the type proposed earlier [8]. As the double bonds of a 1,6-heptadiene interact with each other, there should be more single bond character to these double bonds. This decrease in olefinic character should cause an upfield shift for the vinylic protons.

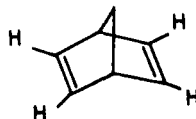
Table 2 lists the  $\delta$  values for the vinyl protons of monomers studied. In none of the monomer systems studied was there any upfield shift of the vinyl protons on comparing the diene with the corresponding monoenes. On the contrary, in each system a small downfield chemical shift occurred on going from the monoene to the diene. This parallels the chemical shift that was observed for the vinyl protons in comparing norbornadiene to norbornene. The vinylic protons shift from 6.01  $\delta$  in norbornene to 6.75  $\delta$  in norbornadiene. Winstein et al. [34] found evidence for excited state electronic interactions only in norbornadiene. Bishof et al. [35] report evidence for electronic interaction in norbornadiene by comparing the ionization potentials

TABLE 2. Nuclear Magnetic Resonance  $\delta$ -Values of Vinyl Protons for Some Unsaturated Hydrocarbons at Ambient Temperatures

Compound		$\delta$ -Values		
XIX	6.16	5.80		
XVIII			5.49	5.33
XVII	6.22	5.84	5.49	5.34
XXIII			5.48	5.28
XXII			5.53	5.35
XXV				4.90
XXIV		5.53	6.36	4.95
XXI				4.96
XV	6.13	5.56		
XX	6.17	5.60		4.98
XIV	6.04		5.57	
XIII			5.54	5.36
XII	6.10		5.56	5.39



6.018



6.758

of the interacting double bonds to the ionization potential of the isolated noninteracting double bond in norbornene. Hoffman [9] proclaimed this technique of photoelectron spectroscopy to be the most direct measure of the degree of interaction of nonconjugated  $\pi$ -electron systems.

If an electronic interaction of the type proposed [8] occurs in 1,6-heptadienes, the degree of interaction should increase as the temperature is decreased. In order to investigate this postulate, variable temperature NMR studies were carried out on four monomer systems as shown in Figs. 1-4. As the temperature was decreased from +150 to  $-50^\circ\text{C}$ , the chemical shifts of the olefinic protons shifted downfield in direct proportion. There was no indication of any electronic interaction occurring which would decrease the olefinic character of the double bonds.

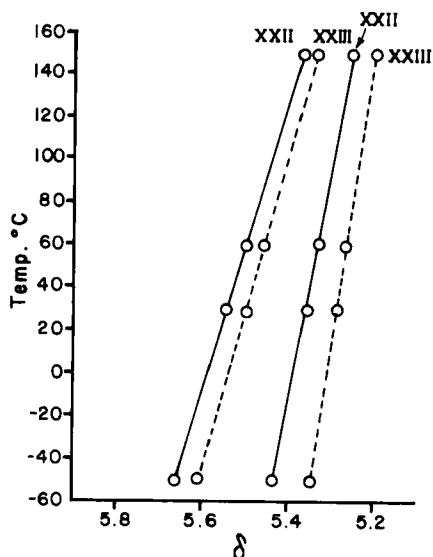
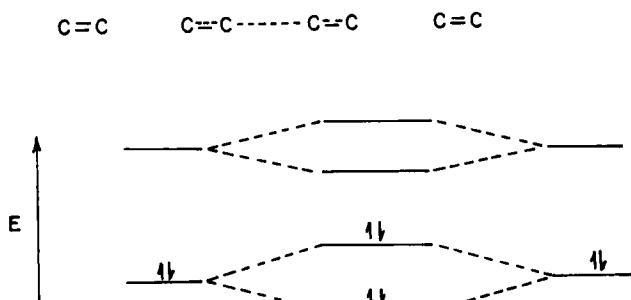


FIG. 1. NMR ( $\delta$ ) values at variable temperature for vinyl protons of 2-phenylallyl ether (XXII) and its corresponding monoene (XXIII). (Samples at temperatures below  $60^\circ\text{C}$  were run as 5% solutions in deuteriochloroform. Samples at  $150^\circ\text{C}$  were run as 2% solutions in hexachloroacetone.)

### Ultraviolet Spectra of the Monomers

Ultraviolet absorption spectroscopy should detect electronic interactions of the type previously proposed [8].

A molecular orbital energy diagram [10] of two interacting non-conjugated double bonds is shown here.





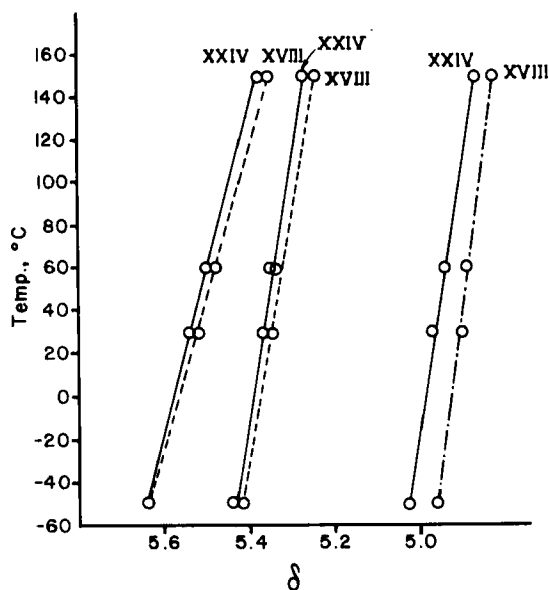


FIG. 2. NMR ( $\delta$ ) values at variable temperature for vinyl protons of 2-phenylallyl methallyl ether (XXIV) and its corresponding monoenes, 2-phenylallyl isobutyl ether (XVIII) and 2-phenyl-n-propyl methallyl ether (XXV). (Samples at temperatures below 60°C were run as 5% solutions in deuteriochloroform. Samples at 150°C were run as 2% solutions in hexachloroacetone.)

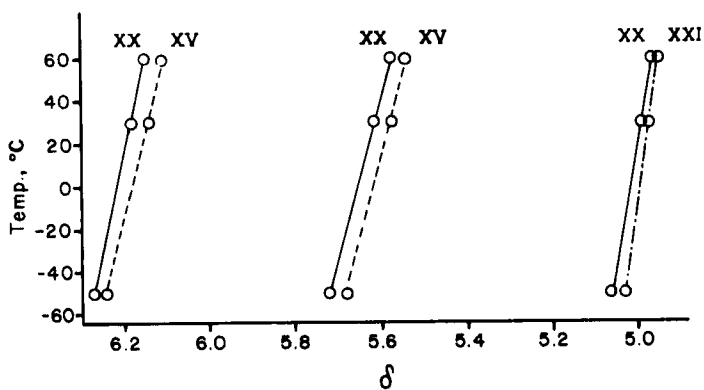


FIG. 3. NMR ( $\delta$ ) values at variable temperature for vinyl protons of methallyl methacrylate (XX) and its corresponding monoenes, isobutyl methacrylate (XV) and methallyl isobutyrate (XXI). (Samples at temperatures below 60°C were run as 5% solutions in deuteriochloroform.)

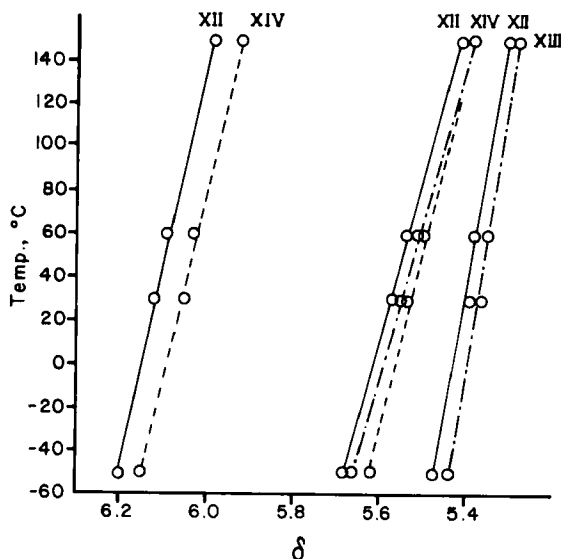


FIG. 4. NMR ( $\delta$ ) values at variable temperature for vinyl protons of 2-phenylallyl methacrylate (XII) and its corresponding monoenes, 2-phenyl-n-propyl methacrylate (XIV) and 2-phenylallyl isobutyrate (XIII). (Samples at temperatures below 60°C were run as 5% solutions in deuteriochloroform. Samples at 150°C were run as 2% solutions in hexachloroacetone.)

The absorption of UV light by a molecule causes an electron to be promoted from the ground state to the excited state. The energy difference between the two states is related to the wavelength of light which will bring about such a transition by the relationship

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

where  $h$  is Planck's constant,  $c$  is the speed of light, and  $\lambda$  is the wavelength of light.

The UV absorption of olefins represents the excitation of an electron from its highest occupied molecular orbital to its lowest unoccupied molecular orbital. The orbitals have been designed  $\pi$  and  $\pi^*$ , respectively. This transition is referred to as a  $\pi \rightarrow \pi^*$  transition.

As can be seen from the molecular orbital energy diagram, the transition from noninteracting double bonds to interacting double bonds should cause a decrease in the energy necessary to promote an electron from the highest occupied molecular orbital to the lowest

TABLE 3. Ultraviolet Absorption Maxima for Monomers Studied in This Work

Compound	$\lambda_{\max}$ (nm)	a (absorptivity coefficient)
XII	238.7	$1.0 \times 10^4$
	200.7	$3.28 \times 10^4$
	182.5	$2.48 \times 10^4$
XIII	238.8	$9.55 \times 10^3$
	200.5	$2.22 \times 10^4$
	182.3	$1.85 \times 10^4$
XIV	203.9	$1.71 \times 10^4$
	187.5	$6.14 \times 10^4$
XV	200.0	$9.57 \times 10^3$
XXI	182.9	$1.05 \times 10^4$
XX	208.7	$8.52 \times 10^3$
	185.3	$1.53 \times 10^4$
XXII	240.8	$2.08 \times 10^4$
	199.8	$4.63 \times 10^4$
	182.7	$4.33 \times 10^4$
XXIII	241.5	$1.04 \times 10^4$
	200.9	$3.10 \times 10^4$
	188.5	$7.50 \times 10^4$
XVIII	239.5	$9.65 \times 10^3$
	198.7	$2.41 \times 10^4$
	178.2	$2.08 \times 10^4$
XXVI	181	$9.98 \times 10^3$
XXIV	240.8	$9.37 \times 10^3$
	197.5	$2.56 \times 10^4$
	183.9	$2.81 \times 10^4$
XIX	195	$9.75 \times 10^3$
XVII	240.0	$8.33 \times 10^3$
	198.5	$2.72 \times 10^4$

vacant molecular orbital. Since the energy is inversely proportional to the wavelength, this would be observed as a bathochromic shift of the absorption maxima or as new longer wavelength absorption. If no interaction occurs in the diene systems, the spectrum of the diene should be the same as a summation of the spectra of the corresponding monoenes.

Table 3 lists the absorption maxima for the dienes and their corresponding monoenes studied in this work. Since it is difficult to compare tabular values, the spectra of these dienes and monoenes as well as the summation spectra of the monoenes have been reproduced in Figs. 5-10.

In none of the dienes studied was there bathochromic shifts nor new longer wavelength absorptions in comparing the dienes with their corresponding monoenes. In Fig. 5 the UV absorption spectra of 2-phenylallyl methacrylate and its corresponding monoenes, 2-phenylallyl isobutyrate, isobutyl methacrylate, and  $\beta$ -phenyl-n-propyl methacrylate, are compared. It is immediately obvious that, as one would expect,  $\beta$ -phenyl-n-propyl methacrylate is not a suitable model monoene for UV studies. The isolated phenyl absorption is entirely different from its absorption when it is in conjugation with the double bond. A more suitable model monoene for UV studies is isobutyl methacrylate. From Fig. 5 it is seen that the summation of the spectrum of isobutyl methacrylate with that of 2-phenylallyl isobutyrate is identical with the spectrum of 2-phenylallyl methacrylate. The

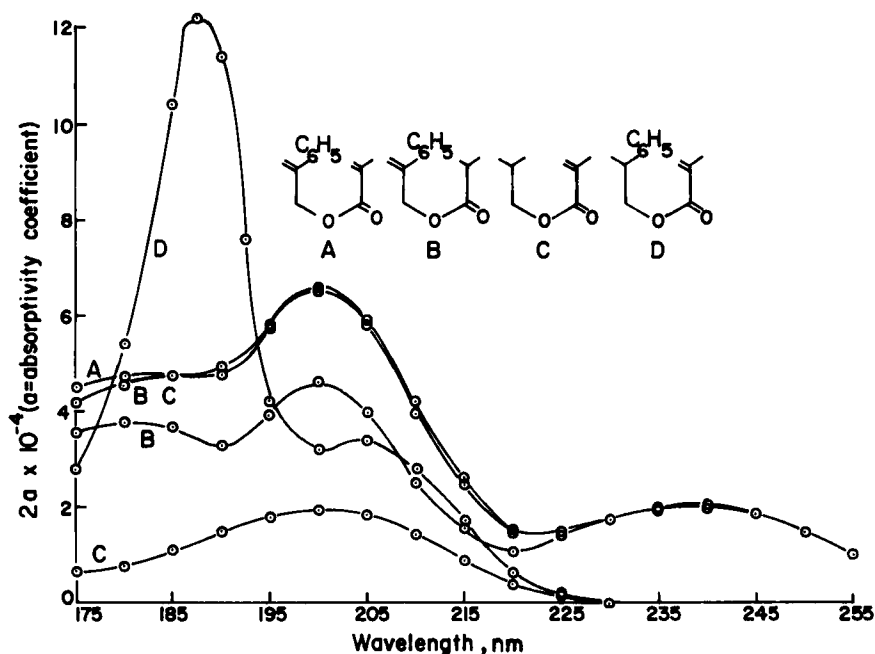


FIG. 5. UV absorption spectra of 2-phenylallyl methacrylate and its corresponding monoenes.

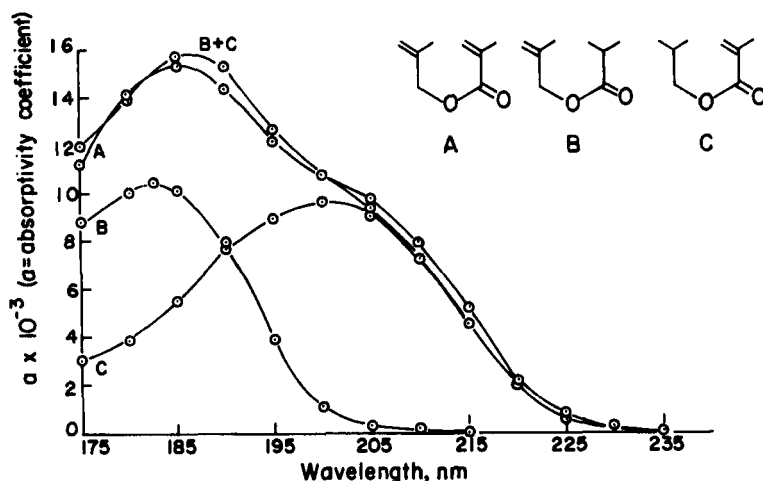


FIG. 6. UV absorption spectra of methallyl methacrylate and its corresponding monoenes.

accepted rule of additivity of the absorbances of noninteracting chromophores has been upheld. There is no indication of electronic interaction in this system.

In Fig. 6 the UV absorption spectra of methallyl methacrylate and its corresponding monoenes methallyl isobutyrate and isobutyl methacrylate are compared. The figure shows that there is essentially complete additivity of the absorbances of the two noninteracting chromophores in methallyl methacrylate. There is no indication of any electronic interaction in this system.

In Fig. 7 the UV absorption spectra of 2-phenylallyl-2'-carboethoxyallyl ether is compared with its corresponding monoenes, 2-phenylallyl isobutyl ether and 2-carboethoxyallyl isobutyl ether. It must be pointed out that the 2-phenylallyl-2'-carboethoxyallyl ether was only 94.5% pure. This impurity was apparently transparent in the UV region under consideration. When the absorption curve of 2-phenylallyl-2'-carboethoxyallyl ether was adjusted to take into consideration the percent purity, the summation curve from the spectrum of 2-phenylallyl isobutyl ether and 2-carboethoxyallyl ether was almost identical (Fig. 8) to the spectrum of the diene. This system also seems to conform to the rule of additivity of absorbance of noninteracting chromophores.

In Fig. 9 the spectrum of 2-phenylallyl ether is compared with the summation spectrum of 2-phenylallyl isobutyl ether. In this system there are no bathochromic shifts, but there is not complete additivity

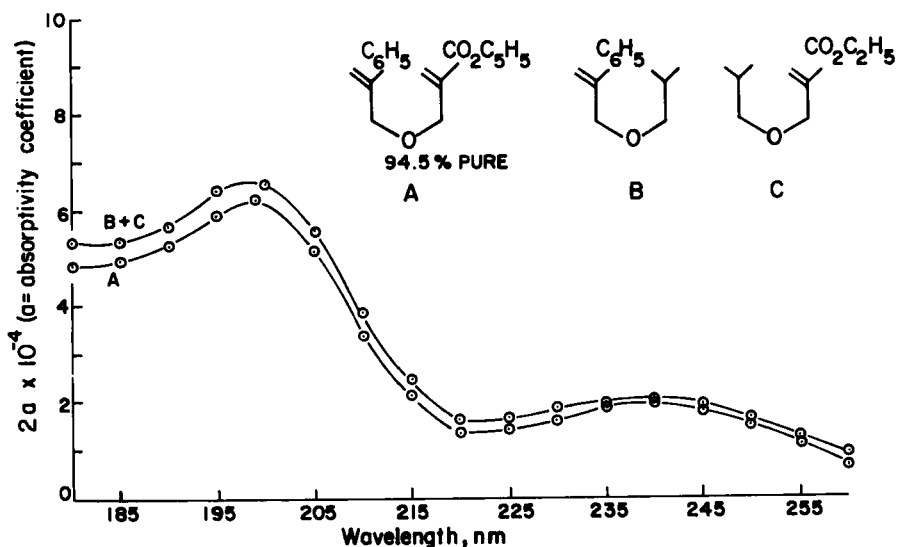


FIG. 7. UV absorption spectra of 2-phenylallyl-2'-carboethoxyallyl ether and its corresponding monoenes.

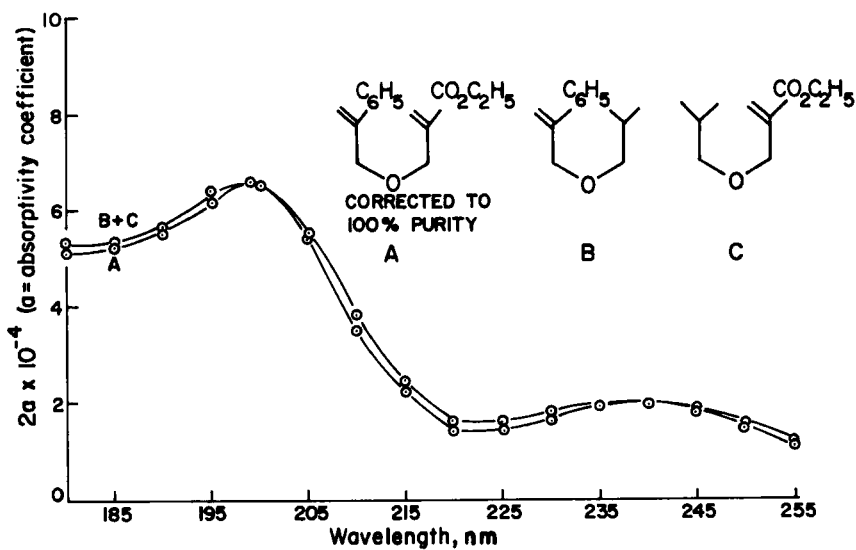


FIG. 8. UV absorption spectra of 2-phenylallyl-2'-carboethoxyallyl ether and its corresponding monoenes.

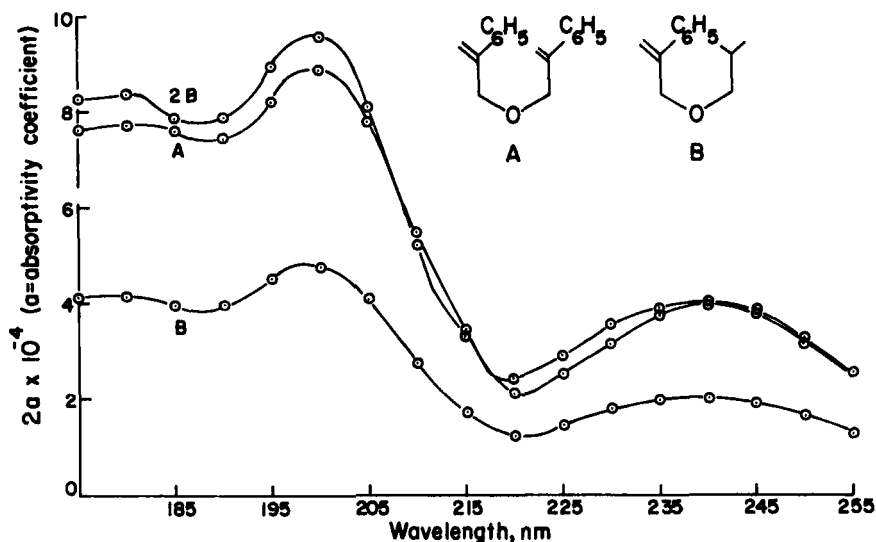


FIG. 9. UV absorption spectra of 2-phenylallyl ether and its corresponding monoenes.

of the two chromophores in the diene. Figure 9 shows that the summation spectrum gives higher absorption in the region from 205 to 175 nm. This deviation is difficult to explain. It is interesting to note that the bands at 240 nm seem to be additive. Such small deviations from the expected have been interpreted in terms of electronic interactions [36]. Since neither the NMR nor IR spectral studies showed any abnormalities in this system, it is doubtful if this anomaly is the result of an interaction of the type previously proposed [8] in which partial ring formation has occurred.

In Fig. 10 the UV absorption spectra of 2-phenylallyl methallyl ether is compared with the absorption spectra of 2-phenylallyl isobutyl ether and methallyl isobutyl ether. The figure shows that there is essentially complete additivity of the two chromophores in the diene when a comparison is made of the diene spectrum with the spectrum prepared by summation of the absorbances of the two monoenes. There is no indication of electronic interaction between the two double bonds of the diene.

In summary, it should be noted that any anomaly in the observed spectra might be evidence for interaction, but UV spectroscopy is a very sensitive tool. Procedural errors or small impurities in samples can cause unexpected and unexplainable results.

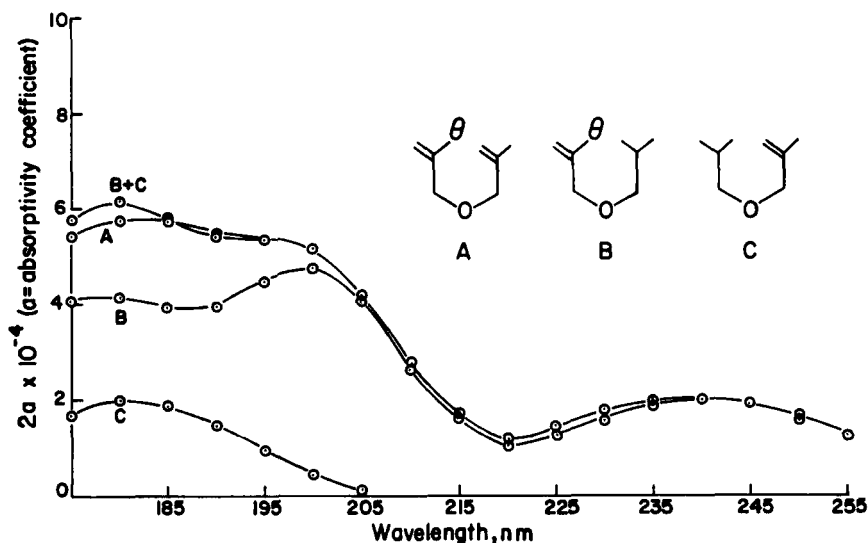


FIG. 10. UV absorption spectra of 2-phenylallyl methallyl ether and its corresponding monoenes.

## EXPERIMENTAL

### Equipment and Data

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. 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. Solution spectra were determined using n-heptane as solvent in 0.01 cm far-UV cells. Nuclear magnetic resonance spectra were obtained on a Varian A-60A Analytical NMR Spectrometer. The chemical shifts were measured in deuteriochloroform and carbon tetrachloride using tetramethylsilane as an internal reference. Infrared spectra were obtained with a Beckman IR-8 Infrared Spectrophotometer or a Beckman IR-10 Infrared Spectrophotometer. 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 and by PCR, Inc., Gainesville, Florida. Molecular distillations were carried out using an Asco Rota-Film Molecular Still.

### Preparation of 2-Phenylallyl Methacrylate (XII)

To a 500-ml, three-necked, round-bottomed flask (in a hood) equipped with stirring bar, condenser, drying tube, and dropping funnel was added 250 ml of dry pyridine, 26.8 g (0.20 mole) 2-phenylallyl alcohol, and 1 g cuprous chloride. To this was added dropwise 23.0 g (0.22 mole) methacrylyl chloride. The solution immediately became bright green. The addition was carried out so that the temperature never exceeded 60°C. The reaction was stirred overnight at room temperature, after which most of the pyridine was stripped off at high vacuum. The residue was poured into water and extracted several times with pentane. The pentane solution was washed with water. After drying over anhydrous magnesium sulfate, the pentane was removed by distillation at atmospheric pressure. The residue was distilled on a molecular still at ~100°/0.10 Torr to give 30 g (74%) of a clear, colorless liquid. Attempted distillation through a 28-in. spinning band column using 2,6-di-tert-butyl-p-cresol resulted in polymerization. Only 4 ml (78°/0.18 mm) was collected before gelation occurred. The product from the molecular still was shown to be 98% pure by GLC;  $n_D^{22}$  1.5335.

The IR spectrum ( $\text{CCl}_4$ ) of the product showed absorption bands at 3100(m), 3075(m), 3040(m), 3000(m), 2975(m), 1950(w), 1890(w), 1800(w), 1720(vs), 1640(s), 1578(w), 1495(m), 1450(s), 1400(vs), 1010(s), 980(w), 940(s), 905(s), and 690(s)  $\text{cm}^{-1}$ .

The NMR spectrum ( $\text{CDCl}_3$ ) gave singlets with hyperfine splitting at 1.94, 5.16, 5.40, 5.58, and 6.12  $\delta$ , and a multiplet centered at 7.40  $\delta$  with area ratios of 3:2:1:2:1:5, respectively.

The UV spectrum (heptane) gave absorptions at 238.8 nm ( $\epsilon = 32,800$ ) and 182.5 nm ( $\epsilon = 24,800$ ).

Analysis: Calculated for  $\text{C}_{13}\text{H}_{14}\text{O}_2$ : C, 77.20; H, 6.97. Found: C, 77.48; H, 6.80.

### Preparation of 2-Phenylallyl Isobutyrate (XIII)

By a procedure essentially the same as for 2-phenylallyl methacrylate, 31.5 g (0.235 mole) 2-phenylallyl alcohol, 250 ml dry pyridine, and 29.8 g (0.28 mole) isobutyryl chloride yielded 31 g (65%) of a clear, colorless liquid, bp 54°C/0.04 Torr,  $n_D^{22}$  1.5128.

Analysis: Calculated for  $\text{C}_{13}\text{H}_{16}\text{O}_2$ : C, 76.43; H, 7.89. Found: C, 76.39; H, 7.43.

The IR spectrum ( $\text{CCl}_4$ ) of the product showed absorption bands at 3100(m), 3080(m), 3040(m), 2990(s), 2950(m), 2890(m), 1950(w), 1875(w), 1805(w), 1735(vs), 1635(m), 1604(w), 1577(w), 1497(m), 1470(s), 1390(s), 1340(m), 1250(s), 1185(s), 1150(vs), 1070(m), 1030(w), 1005(w), 980(m), 905(s), and 695(s)  $\text{cm}^{-1}$ .

The NMR spectrum ( $\text{CDCl}_3$ ) gave a doublet centered at 1.13  $\delta$  a multiplet centered at 2.56  $\delta$ ; singlets with hyperfine splitting at 5.00, 5.36, and 5.54  $\delta$ ; and a multiplet centered at 7.36  $\delta$  with area ratios of 6:1:2:1:1:5, respectively.

### Preparation of $\beta$ -Phenyl-n-propyl Alcohol (XVI)

This reaction was carried out in a hood. To a 2-liter, three-necked, round-bottomed flask equipped with a nitrogen inlet, magnetic stirring bar, drying tube, and dropping funnel was added 236 g (2.0 moles)  $\alpha$ -methylstyrene, 500 ml dry diglyme, and 25 g (0.9 mole) of freshly ground sodium borohydride. This was cooled to 0°C with an ice bath and flushed with nitrogen. While the temperature and nitrogen flow were held constant, 100 g (1.35 moles) of freshly distilled boron trifluoride-etherate (61°C/30 Torrs) was added dropwise. After the addition was completed, stirring was continued under nitrogen for 1 hr. Then the ice bath was removed and stirring was continued for an additional hour. At that time, 15 ml ethylene glycol was added cautiously to destroy unreacted sodium borohydride. This was followed by the addition of 30 g sodium hydroxide. Caution! Then 272 g of 30% hydrogen peroxide was added dropwise very slowly at 0°C. The contents were allowed to stir overnight.

The next day, 500 ml water was added, and the solution was extracted with six 250-ml portions of pentane. The combined pentane extract was washed three times with an equal volume of water and dried over anhydrous magnesium sulfate. The pentane was removed by distillation at atmospheric pressure. The residue was distilled at ~56°C/0.25 Torr to yield 213 g (78.5%) of a clear, colorless liquid,  $n_D^{24}$  1.5256.

The IR spectrum (neat) of the product showed absorption bands at 3360(broad, s), 3100(w), 3080(w), 3040(m), 2970(s), 2940(s), 2890(s), 1955(w), 1875(w), 1810(w), 1605(m), 1495(s), 1450(s), 1380(w), 1230(w), 1190(w), 1090(w), 1065(m), 1035(s), 1010(s), 975(w), 905(w), 760(s), and 695(s)  $\text{cm}^{-1}$ .

The NMR spectrum ( $\text{CDCl}_3$ ) showed a doublet centered at 1.22  $\delta$ , a broad resonance signal at 2.28  $\delta$ , a multiplet centered at 2.79  $\delta$ , a doublet centered at 3.50  $\delta$ , and a singlet at 7.83  $\delta$  with area ratios of 3:1:1:2:5, respectively.

### Preparation of $\beta$ -Phenyl-n-propylmethacrylate (XIV)

By essentially the same procedure as was used for 2-phenylallyl methacrylate, 27.2 g (0.20 mole)  $\beta$ -phenyl-n-propyl alcohol, 1 g CuCl, 200 ml dry pyridine, and 22.9 g (0.22 mole) methacrylyl chloride yielded 22 g (54%) of a liquid shown to be 98% pure by GLC ( $n_D^{22}$

1.5055) after purification by passing through a 20-cm chromatography column containing 10 cm of florex and 10 cm of activity V Woelm silica gel, using pentane as the eluent, followed by distillation through a molecular still.

The IR spectrum ( $\text{CCl}_4$ ) of the product showed absorption bands at 3100(w), 3080(m), 3040(m), 2980(s), 1950(w), 1880(w), 1805(w), 1720(vs), 1640(s), 1605(w), 1495(m), 1450(s), 1400(m), 1390(w), 1370(m), 1320(s) and 1295(s, doublet), 1165(vs), 1070(w), 1010(s), 990(m), 935(s), 693(s), and 650(w)  $\text{cm}^{-1}$ .

The NMR spectrum ( $\text{CDCl}_3$ ) showed a doublet centered at 1.33  $\delta$ , a singlet with hyperfine splitting at 1.91  $\delta$ , a multiplet centered at 3.15  $\delta$ , a doublet centered at 4.24  $\delta$ , a singlet with hyperfine splitting at 5.53  $\delta$ , a singlet with hyperfine splitting at 6.06  $\delta$ , and a singlet at 7.28  $\delta$  with area ratios of 3:3:1:2:1:1:5, respectively.

The UV spectrum (heptane) gave absorption bands at 203.9 nm ( $\epsilon = 17,100$ ) and 187.5 nm ( $\epsilon = 61,400$ ). Analysis: Calculated for  $\text{C}_{13}\text{H}_{16}\text{O}_2$ : C, 76.43; H, 7.89. Found: C, 76.15; H, 8.16.

### Preparation of Isobutylmethacrylate (XV)

By essentially the same procedure as used for 2-phenylallyl methacrylate, 14.8 g (0.20 mole) isobutyl alcohol, 200 ml dry pyridine, 1 g cuprous chloride, and 23 g (0.22 mole) methacrylyl chloride give 19 g (67% yield) of a clear, colorless product, bp 155°C/760 Torrs. Reported [37] 155°C/760 Torrs.

### Preparation of Ethyl- $\alpha$ -(hydroxymethyl)acrylate

This compound was prepared according to the procedure of Rosenthal, Schwartzman, Greco, and Proper [32]. The reaction was carried out in a very good hood since nickel carbonyl is extremely toxic. Into a 2-liter, round-bottomed flask equipped with a mechanical stirrer, thermometer, Dry Ice cooled condenser, and dropping funnel were placed 10 g hydroquinone, 700 ml 95% ethanol, 120 g (2 moles) acetic acid, and 86 g (0.50 mole) nickel carbonyl. The solution was stirred and heated to 55°C. Through a dropping funnel 2 ml of 112 g (2 moles) propargyl alcohol was added, and the solution was allowed to stir until the color darkened and an exotherm was observed (2 min).

At this point the heating mantel was removed, and the remainder of the propargyl alcohol was added dropwise at such a rate that the refluxing was under control. The addition required about 40 min, and the temperature reached 75 to 81°C at the end of the addition. The solution was allowed to stir for 30 min, and then 28 ml (0.5 mole) concentrated sulfuric acid was added slowly with stirring. The flask then contained the precipitated nickel sulfate hexahydrate and a yellow liquid phase. The contents were filtered under reduced pressure through a bromine trap into a 5-liter, round-bottomed flask. Concentrated sulfuric acid (10 ml) was added, and the solution was refluxed for 7 hr through a Soxhlet extractor containing anhydrous magnesium sulfate.

The reaction solution was cooled, and 106 ml 5 N sodium hydroxide was added to neutralize the acid catalyst. The mixture was then distilled under reduced pressure until bumping became vigorous. At this point, twice the volume of water was added, and the solution was extracted with three 400-ml portions of chloroform. The solution was dried, and the solvent was stripped off at atmospheric pressure. The liquid residue was fractionally distilled through a 28-in. spinning band column to give 77 g (29.6%) of a clear liquid, bp 72.5°C/1.5 Torrs,  $n_D^{22}$  1.4454.

#### Preparation of Ethyl- $\alpha$ -chloromethyl)acrylate

This compound was prepared according to the procedure of the Koppers Co. [33]. To a 250-ml, round-bottomed flask equipped with a condenser and stirring bar was added 7 g (0.048 mole) cuprous chloride and 100 ml (1.2 moles) concentrated hydrochloric acid. To this was added 0.2 g hydroquinone and 55 ml (0.4 mole) ethyl-( $\alpha$ -hydroxymethyl)acrylate. The solution was stirred overnight at room temperature. The two-phase system was diluted with an equal volume of water and extracted with two 250-ml portions of chloroform. The chloroform solution was dried and stripped of solvent at atmospheric pressure. The liquid residue distilled at 63°C/9.5 Torrs to give 45 g (75.6%) of ethyl-( $\alpha$ -chloromethyl)acrylate;  $n_D^{20}$  1.4496.

#### Preparation of 2-Phenylallyl-2'-carboethoxyallyl Ether (XVII)

This reaction was carried out in a hood. The apparatus was set up as described in the preceding ether preparation. In the normal manner, 5.3 g (0.11 mole) of 50% sodium hydride was added to the reaction vessel, and the mineral oil was removed. Then 125-ml dry dimethyl sulfoxide was added carefully. To this was added dropwise

13.4 g (0.10 mole) 2-phenylallyl alcohol. The solution was stirred for 3 hr. Then the sodium alkoxide dimethyl sulfoxide solution was transferred to an addition funnel and added dropwise to 14.8 g (0.10 mole) ethyl  $\alpha$ -(chloromethyl)acrylate in 50-ml dry dimethyl sulfoxide. The addition was carried out at such a rate that the temperature did not exceed 35°C. After the addition had been completed, the reaction medium was stirred an hour. At the end of this period, the reaction mixture was worked up in the usual manner. The product was distilled through a molecular still at 120°C/0.005 Torr to give 15 g (61%) of a clear, colorless liquid,  $n_D^{22}$  1.5139.

Gas chromatographic analysis using a 9 ft, 30% SE 30 column at 230°C with the injector at 280°C indicated the product to be ~94.5% pure. Attempts to fractionally distill the product under full vacuum resulted in polymerization even in the presence of inhibitors.

Analysis: Calculated for  $C_{15}H_{18}O_3$ : C, 73.12, H, 7.37. Found: C, 73.90; H, 7.96.

The IR spectrum (neat) of the product gave absorptions at 3080(w), 3050(w), 3020(w), 2975(m), 2920(w), 2860(m), 1950(w), 1885(w), 1800(w), 1720(vs), 1630(m), 1600(w), 1570(w), 1492(w), 1440(m), 1380(m), 1300(s), 1360(s), 1160(s, doublet), 1100(vs, doublet), 1020(m), 940(m), 900(m), 810(m), 770(s), and 700(s)  $cm^{-1}$ .

The NMR spectrum ( $CCl_4$ ) gave a triplet centered at 1.30  $\delta$ , a multiplet centered at 4.16  $\delta$ , a singlet at 4.38  $\delta$ , a singlet with hyperfine splitting at 5.34  $\delta$ , a singlet at 5.49  $\delta$ , a singlet with hyperfine splitting at 5.84  $\delta$ , a singlet with hyperfine splitting at 6.22  $\delta$ , and a multiplet centered at 7.31  $\delta$  with area ratios of 3:4:2:1:1:1:1:5, respectively.

The UV spectrum (heptane) gave absorption bands at 240.0 nm ( $\epsilon = 8.330$ ) and 198.5 nm ( $\epsilon = 27,200$ ).

### Preparation of 2-Phenylallyl Isobutyl Ether (XVIII)

By essentially the same procedure as used for 2-phenylallyl-2'-carboethoxyallyl ether, 10.6 (0.22 mole) of 50% sodium hydride, 250 ml of dry dimethyl sulfoxide, 16.3 g (0.22 mole) of dry isobutyl alcohol, and 30.5 g (0.20 mole) of 2-phenylallyl chloride gave 34 g (89.5%) of a clear liquid, bp 70°C/0.7 Torr,  $n_C^{22}$  1.5086.

The IR spectrum ( $CCl_4$ ) of the product showed absorption bands at 3100(m), 3075(m), 3045(m), 2970(vs), 2875(vs), 1950(w), 1880(w), 1820(w), 1730(w), 1630(m), 1600(w), 1575(w), 1495(m), 1470(s), 1385(w), 1370(m), 1300(w), 1120(s), 1085(vs), 1020(m), 900(s), and 695(s)  $cm^{-1}$ .

The NMR spectrum ( $CDCl_3$ ) showed a doublet centered at 0.89  $\delta$ , a multiplet at 1.88  $\delta$ , a doublet centered at 3.25  $\delta$ , a singlet with

hyperfine splitting at 4.34  $\delta$ , a singlet with hyperfine splitting at 5.33  $\delta$ , a singlet with hyperfine splitting at 5.49  $\delta$ , and a multiplet centered at 7.37  $\delta$  with area ratios of 6:1:2:2:1:1:5, respectively.

The UV spectrum (heptane) gave absorption bands at 239.5 nm ( $\epsilon = 9,650$ ), 198.8 nm ( $\epsilon = 24,100$ ), and 178.3 nm ( $\epsilon = 20,800$ ).

Gas chromatographic analysis using a 9 ft, 30% Carbowax 20 M column with column temperature at 200°C and injector temperature at 240°C indicated the product to be of about 99% purity.

Analysis: Calculated for  $C_{13}H_{18}O$ : C, 82.05; H, 9.53. Found: C, 81.82; H, 9.30.

### Preparation of 2-Carboethoxyallyl Isobutyl Ether (XIX)

By essentially the same procedure as used for 2-phenylallyl-2'-carboethoxy allyl ether, 4.32 g (0.090 mole) of 50% sodium hydride, 100 ml of dry dimethyl sulfoxide, 6.7 g (0.090 mole) dry isobutyl alcohol, and 13 g (0.087 mole) ethyl  $\alpha$ -chloromethyl acrylate in 50 ml dry dimethyl sulfoxide gave 9.8 g (60%) of a clear colorless liquid, bp 59°C/1.7 Torr.

Gas chromatographic analysis using a 9 ft 30% Carbowax 20 M column at 150°C with the injector at 220°C indicated the product to be 100% pure.

Analysis: Calculated for  $C_{10}H_{18}O_3$ : C, 64.68; H, 9.74. Found: C, 64.53; H, 9.55.

The IR spectrum (neat) of the product showed absorption bands at 2970(s), 2920(w), 2880(s), 2820(w), 2740(w), 1720(s), 1640(m), 1470(s), 1385 and 1370(s), 1305 and 1270(s), 1170 and 1105(vs), 1030(s), 950(s), 860(w), 820(m), 685(w), and 650(w)  $cm^{-1}$ .

The NMR spectrum ( $CCl_4$ ) showed a doublet centered at 0.9  $\delta$ , a triplet centered at 1.28  $\delta$ , a septet centered at 1.87  $\delta$ , a doublet centered at 3.21  $\delta$ , a quartet centered at 4.16  $\delta$  overlapping a singlet with hyperfine splitting centered at 4.10  $\delta$ , a singlet with hyperfine splitting at 5.80  $\delta$ , and a singlet with hyperfine splitting centered at 6.16  $\delta$  with area ratios of 6:3:1:2:2:2:1:1, respectively.

The UV spectrum (iso-octane) gave an absorption band at 196 nm ( $\epsilon = 9,700$ ).

### Preparation of 2-Phenylallyl Ether (XXII)

By essentially the same procedure used for 2-phenylallyl-2'-carboethoxyallyl ether, 10.6 g (0.22 mole) of 50% sodium hydride, 250 ml of dry dimethyl sulfoxide, 26.8 g (0.20 mole) of 2-phenylallyl alcohol, and 30.5 g (0.20 mole) 2-phenylallyl chloride gave 48.5 g (97%) of a slightly yellow, clear liquid, bp 110°C/0.010 Torr. This

product was shown to have no detectable impurities by vapor phase chromatography. The 2-phenylallyl ether was redistilled using 2,6-di-tert-butyl-p-cresol as inhibitor to give a clear, colorless liquid product, bp 135-137°C/0.40 Torr,  $n_D^{22}$  1.5876.

The IR spectrum ( $\text{CCl}_4$ ) of the product showed absorption bands at 3100(s), 3070(s), 3040(s), 2860(s), 1950(w), 1880(w), 1820(m), 1630(s), 1600(m), 1575(m), 1495(s), 1445(m), 1310(m), 1125(s), 1075(vs), 1025(s), 900(s), and 690(s)  $\text{cm}^{-1}$ .

The NMR spectrum ( $\text{CDCl}_3$ ) showed a singlet at 4.43  $\delta$ , a singlet with hyperfine splitting at 5.37  $\delta$ , a singlet at 5.55  $\delta$ , and a multiplet centered at 7.37  $\delta$  with area ratios of 2:1:1:5, respectively.

The UV spectrum (heptane) gave absorption bands at 240.8 nm ( $\epsilon = 20,800$ ), 199.8 nm ( $\epsilon = 46,300$ ), and 182.7 nm ( $\epsilon = 43,300$ ).

Analysis: Calculated for  $\text{C}_{18}\text{H}_{18}\text{O}$ : C, 86.35; H, 7.25. Found: C, 86.54; H, 6.96.

#### Preparation of 2-Phenylallyl-2'-phenyl-n-propyl Ether (XXIII)

By essentially the same procedure previously used for 2-phenylallyl-2'-carboethoxyallyl ether, 10.6 g (0.22 mole) 50% sodium hydride, 250 ml. of dry dimethyl sulfoxide, 27.2 g (0.20 mole) 2-phenyl-n-propyl alcohol, and 30.5 g (0.20 mole) of 2-phenylallyl chloride gave 2-phenylallyl-2'-phenyl-n-propyl ether which was distilled at 128°C/0.70 Torr to give 41.7 g (83%) of clear, colorless product,  $n_D^{22}$  1.5624.

The IR spectrum ( $\text{CCl}_4$ ) of the product showed absorption bands at 3100(s), 3080(s), 3040(s), 2980(s), 2870(s), 1950(w), 1870(w), 1810(w), 1630(m), 1603(m), 1575(w), 1495(s), 1450(s), 1375(m), 1300(m), 1120(s), 1085(vs), 1025(m), 905(s), and 692(s)  $\text{cm}^{-1}$ .

The NMR spectrum ( $\text{CDCl}_3$ ) showed a doublet centered at 1.28  $\delta$ , a multiplet centered at 3.05  $\delta$ , a doublet with hyperfine splitting centered at 3.57  $\delta$ , a singlet at 4.35  $\delta$ , a singlet with hyperfine splitting at 5.30  $\delta$ , a singlet at 5.50  $\delta$ , and a multiplet centered at 7.32  $\delta$  with area ratios of 3:1:2:2:1:1:10, respectively.

The UV spectrum (heptane) gave absorption bands at 241.5 nm ( $\epsilon = 10,400$ ), 200.9 nm ( $\epsilon = 31,000$ ), and 188.5 nm ( $\epsilon = 75,000$ ).

Analysis: Calculated for  $\text{C}_{18}\text{H}_{20}\text{O}$ : C, 85.67; H, 7.98. Found: C, 85.47; H, 7.91.

#### Preparation of 2-Phenylallylmethyl Ether (XXIV)

By essentially the same procedure used for 2-phenylallyl-2'-carboethoxyallyl ether, 10.6 g (0.22 mole) of 50% sodium hydride,

250 ml of dry dimethyl sulfoxide, 15.8 g (0.22 mole) of dry methallyl alcohol, and 30.5 g (0.20 mole) of 2-phenylallyl chloride yielded 33.8 g (90%) of a clear, colorless liquid,  $n_D^{22}$  1.5287, bp 129–132°C/20

Torr. Gas chromatography analysis using a 9 ft, 30% SE column at 190°C indicated the product to be of 99% purity.

Analysis: Calculated for  $C_{13}H_{16}O$ : C, 82.92; H, 8.57. Found: C, 83.18; H, 8.99.

The IR spectrum ( $CCl_4$ ) of the product showed absorption bands at 3100(m), 3080(w), 3040(w), 2990(m), 2930(m), 2860(s), 1950(w), 1880(w), 1820(w), 1660(m), 1635(m), 1600(w), 1575(w), 1495(m), 1445(m), 1375(w), 1350(w), 1305(w), 1250(w), 1120(s), 1080(vs), 1030(w) 900(s), and 695(s)  $cm^{-1}$ .

The NMR spectrum ( $CDCl_3$ ) showed a singlet with hyperfine splitting at 1.73  $\delta$ , a singlet at 3.94  $\delta$ , a singlet with hyperfine splitting at 5.35  $\delta$ , a broad absorption with hyperfine splitting at 4.94  $\delta$ , an absorption with hyperfine splitting at 5.35  $\delta$ , a singlet with hyperfine splitting at 5.50  $\delta$ , and a multiplet centered at 7.36  $\delta$  with area ratios of 3:2:2:2:1:1:5, respectively.

The UV spectrum (heptane) gave absorption bands at 240.6 nm ( $\epsilon = 9,370$ ), 197.5 nm ( $\epsilon = 25,600$ ), and 183.9 nm ( $\epsilon = 28,100$ ).

### Preparation of $\beta$ -Phenyl-n-propyl Methallylether (XXV)

By essentially the same procedure used for 2-phenylallyl-2'-carboethoxyallyl ether, 10.6 g (0.22 mole) of 50% sodium hydride, 200 ml of dry dimethyl sulfoxide, 27.2 g (0.20 mole) of  $\beta$ -phenyl-n-propyl alcohol, and 23.1 g (0.20 mole) of methallyl chloride yielded 33.5 g (88.5%) of a clear, colorless liquid,  $n_D^{22}$  1.4978, bp 65–68°C/0.65 Torr.

The IR spectrum ( $CCl_4$ ) of the product showed absorption bands at 3095(m), 3080(m), 3040(m), 2980(s), 2860(s), 1945(w), 1870(w), 1805(w), 1660(m), 1605(m), 1495(m), 1450(m), 1450(s), 1375(m), 1350(w), 1250(w), 1100(vs), 1020(m), 980(s), and 695(s)  $cm^{-1}$ .

The NMR spectrum ( $CDCl_3$ ) showed a doublet centered at 1.30  $\delta$ , a singlet with hyperfine splitting at 1.68  $\delta$ , a multiplet centered at 3.07  $\delta$ , a doublet with hyperfine splitting centered at 3.49  $\delta$ , a singlet at 3.86  $\delta$ , a singlet at 4.89  $\delta$ , and a singlet at 7.25  $\delta$  with area ratios of 3:3:1:2:2:5, respectively.

The UV spectrum (heptane) gave absorption bands at 206.0 nm ( $\epsilon = 8,630$ ) and 188.1 nm ( $\epsilon = 62,700$ ).

Analysis: Calculated for  $C_{13}H_{18}O$ : C, 82.06; H, 9.54. Found: C, 81.84; H, 9.44.



### Preparation of Methallyl Isobutyl Ether (XXVI)

To a 500-ml, three-necked, round-bottomed flask equipped with stirring bar, nitrogen inlet, and condenser was added 200 ml of dry isobutyl alcohol followed by 10.5 g (0.457 mole) of clean sodium metal. The temperature was increased until refluxing had begun. The system was left in this state overnight. The next morning the sodium had all reacted, leaving a clear solution. To the alkoxide solution was added dropwise 36.2 g (0.40 mole) methallyl chloride. The reaction was stirred under reflux overnight. The next morning the milky-white solution was allowed to cool and then was worked up in the usual manner. The product was separated from the isobutyl alcohol by distillation. The yield of product boiling at 127°C was only 10 g (19.5%),  $n_D^{24}$  1.4156. Reported [38], bp 129.8–130.8°C.

The IR absorption spectrum (neat) gave absorption bands at 3090(w), 2970(s), 2880(s), 1660(m), 1450(m), 1360(w), 1260(w), 1100(s), 980(w), and 900(s)  $\text{cm}^{-1}$ .

The NMR spectrum ( $\text{CDCl}_3$ ) gave a doublet centered at 0.92  $\delta$ , a singlet at 1.75  $\delta$ , a multiplet centered at 1.88  $\delta$ , a doublet centered at 3.18  $\delta$ , a singlet at 3.88  $\delta$ , and a broad absorption at 5.08  $\delta$  with area ratios of 6:3:1:2:2:2, respectively.

The UV spectrum (heptane) gave an absorption at 181 nm ( $\epsilon = 9,980$ ).

### Preparation of Methallyl Methacrylate (XX)

By essentially the same procedure used for 2-phenylallyl methacrylate, 300 ml dry pyridine, 14.4 g (0.2 mole) methallyl alcohol, and 209 g (0.20 mole) methacrylyl chloride gave methallyl methacrylate, bp 38°C/5 Torr;  $n_D^{20}$  1.4412. Reported [39], bp 70°C/25 Torr,  $n_D^{20}$  1.4386.

The NMR spectrum ( $\text{CDCl}_3$ ) gave a singlet with hyperfine splitting at 1.78  $\delta$ , a singlet with hyperfine splitting at 1.97  $\delta$ , a singlet with hyperfine splitting at 4.58  $\delta$ , a broad absorption at 4.97  $\delta$ , an absorption with hyperfine splitting at 5.57  $\delta$ , and an absorption also with hyperfine splitting at 6.14  $\delta$  with area ratios of 3:3:2:2:1:1, respectively.

The UV spectrum (heptane) gave absorptions at 208.75 nm ( $\epsilon = 8,520$ ) and 185.25 nm ( $\epsilon = 15,300$ ).

### Preparation of Methallyl Isobutyrate (XXI)

By essentially the same procedure used for 2-phenylallyl methacrylate, 14.4 g (0.2 mole) methallyl alcohol, 120 ml dry pyridine, 23 g (0.22 mole) isobutyryl chloride gave 22 g (77.5%) of a clear,

colorless liquid product, bp 150°C/atm. The reported [40] boiling point is 150°C.

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