[CONTRIBUTION FROM THE PURDUE RESEARCH FOUNDATION AND DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

THE ULTRAVIOLET SPECTRA OF CHLORINE-CONTAINING CYCLOPENTENES AND CYCLOPENTADIENES

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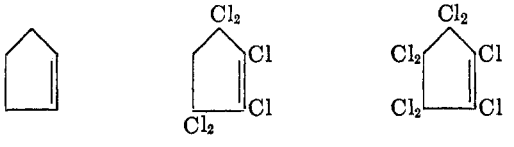
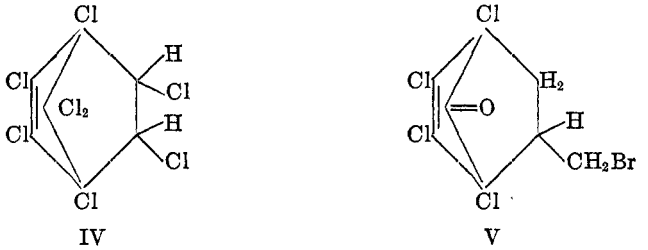
In connection with structural studies carried out in this laboratory, it was necessary to examine the ultraviolet absorption of a series of chlorine-containing cyclopentenes and cyclopentadienes. The auxochromic effect of chlorine substituents on the absorption spectra of five-membered, carbocyclic olefins has received very limited attention. McBee, Smith, and Ungnade (1) have shown that the allylic chlorine substituent in the cyclopenten-3-ones confers a bathochromic (red) shift of 6 mμ to the λ_{max} whereas in the vinylic positions it causes a 10 mμ red shift corresponding to that observed in the aliphatic series on going from ethylene (λ_{max} 175 mμ) to vinyl chloride (λ_{max} 185 mμ) (2). Our data on cyclopentenes conform to those above. Whereas cyclopentene itself (I) absorbs outside the range of the quartz instrument (λ_{max} 185 mμ) (3), 1,2,3,3,5,5-hexachlorocyclopentene (I) (λ_{max} 224 mμ) and octachlorocyclopentene (III) (λ_{max} 230 mμ) both have a single absorption band in an accessible region (Fig. 1). Accepting the value of 10 mμ for the red shift conferred by a vinylic chlorine atom, the corresponding shift due to each allylic chlorine atom is readily cal-



I II III

culated as slightly less than 5 mμ, and for the two chlorine atoms and the non-allylic methylene group in III, the shift per chlorine atom is calculated as 3 mμ.

The absorption of chlorine-containing bicyclic olefins was examined but in this case ring strain is apparently a complicating factor. For 1,2,3,4,5,6,7,7-octachlorobicyclo[2.2.1]hept-2-ene (IV) the observed λ_{max} is only 212 mμ (Fig. 2) whereas if the molecule is considered as an octachloro-3,5-ethanocyclopentene



IV V

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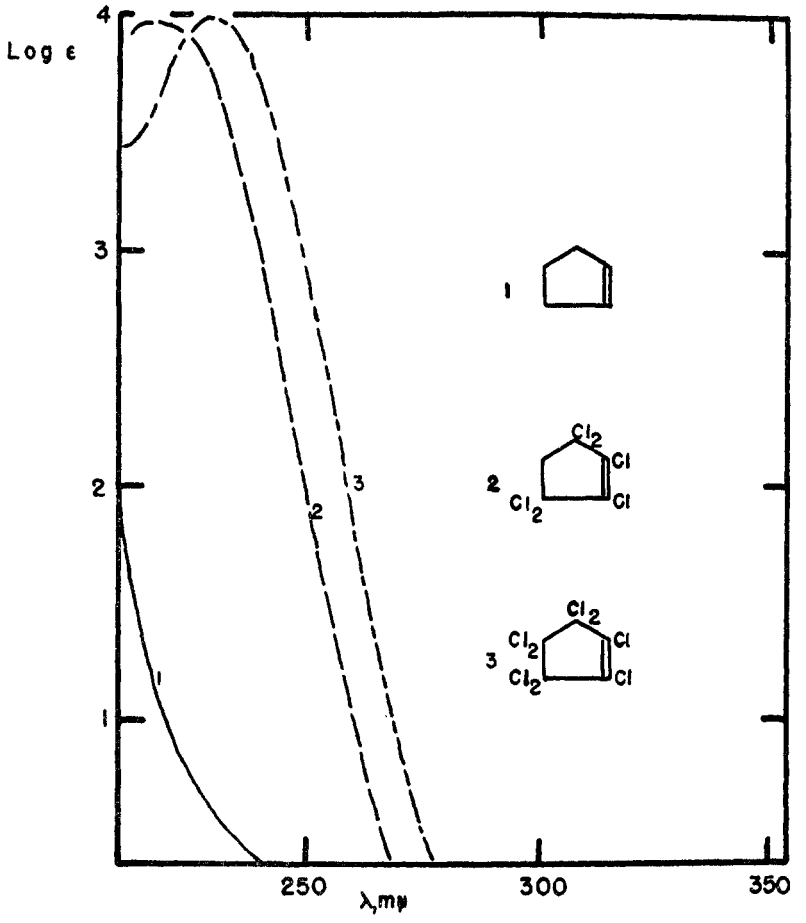
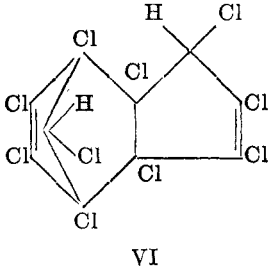


FIG. 1. ULTRAVIOLET SPECTRA IN ETHANOL: ——— Cyclopentene, - - -1,2,3,3,5,5-Hexachlorocyclopentene, — - — -Octachlorocyclopentene.

and the λ_{max} is calculated on this basis [allowing, by Woodward's rules (4), 5 mμ for the 3- and 5-alkyl substituents] the value obtained is λ_{max} 231 mμ. For 5 - bromomethyl - 1,2,3,4 - tetrachlorobicyclo[2.2.1]hept - 2 - ene - 7 - one (V), λ_{max} (obs.) is 210 mμ whereas λ_{max} (calc'd) is 225 mμ (disregarding the carbonyl group). Unfortunately, ultraviolet spectral data are not available for the parent



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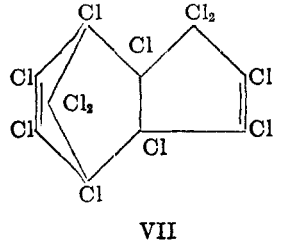

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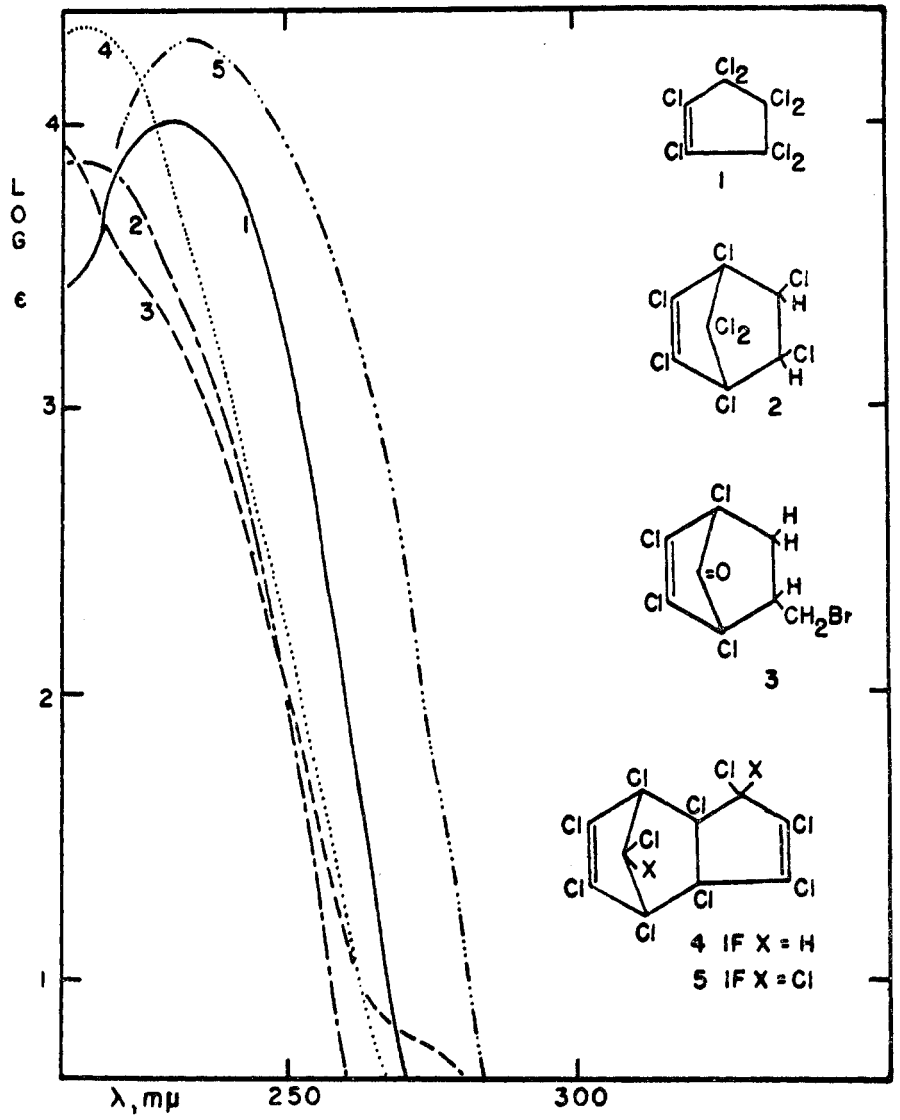


FIG. 2. ULTRAVIOLET SPECTRA IN *n*-HEXANE: ————Octachlorocyclopentene, - — - — 1,2,3,4,5,6,7,7-Octachlorobicyclo[2.2.1]hept-2-ene, ----------5-Bromomethyl-1,2,3,4-tetrachlorobicyclo[2.2.1]hept-2-en-7-one, ····· 1,2,3,3a,4,5,6,7,7a,8-decachloro-3a,4,-7,7a-tetrahydro-4,7-methanoindene, - ••• – ••• Perchloro-3a,4,7,7a-tetrahydro-4,7-methanoindene.

hydrocarbon. A much better correlation obtains with 1,2,3,3a,4,5,6,7,7a,8-decachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (VI) (λ_{max} 223 mμ) and the corresponding chlorocarbon (VII) (λ_{max} 232 mμ) (Fig. 2). Proceeding as above, the calculated values for λ_{max} for VI and VII are 225–227 mμ and 230 mμ respectively. Good correlation of absorption intensity was observed on going from mono- to di-chromophoric molecules.

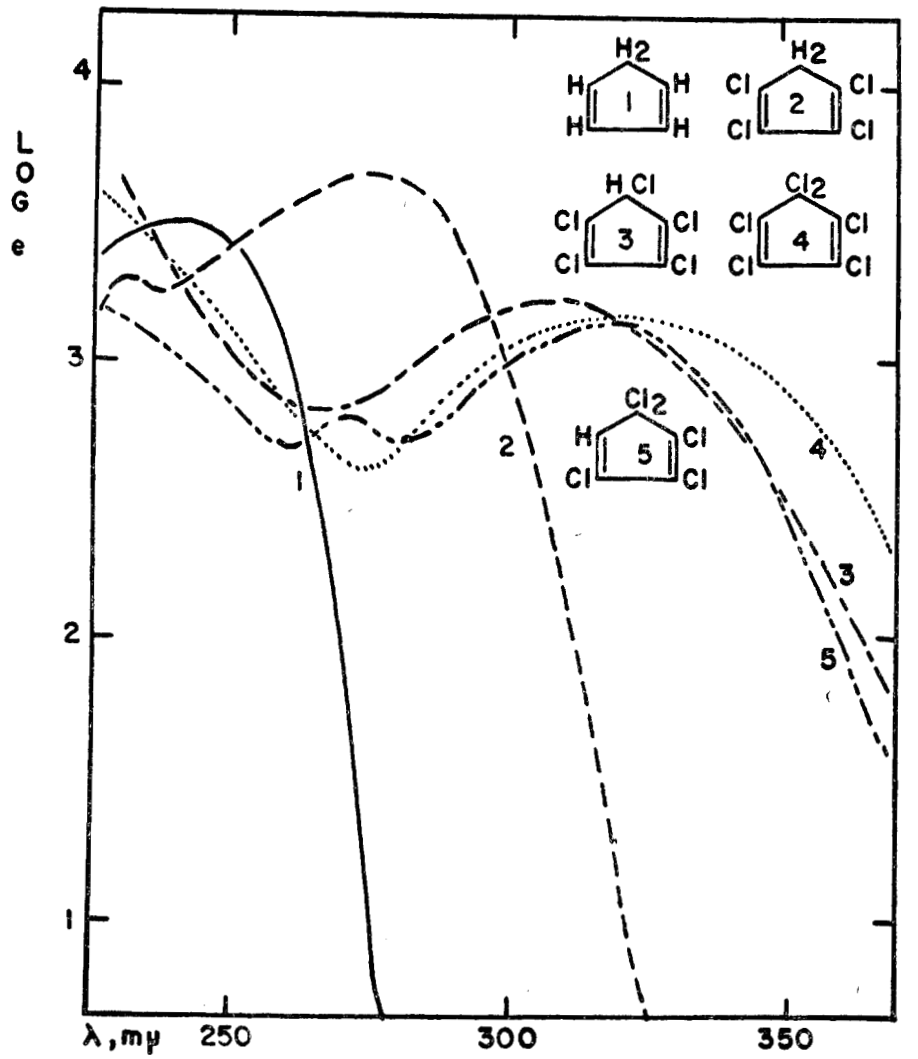
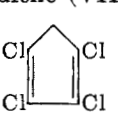


FIG. 3. ULTRAVIOLET SPECTRA IN ETHANOL: ———Cyclopentadiene, — — —1,2,3,4-Tetrachlorocyclopentadiene, — · — -1,2,3,4,5-Pentachlorocyclopentadiene, ····· Hexachlorocyclopentadiene. — -- — -- — --2,3,4,5,5-Pentachlorocyclopentadiene.

In the cyclopentadiene series, the bathochromic shift of 10 mμ per vinylic chlorine atom still holds, whereas in the aliphatic series a red shift of only 6 mμ is observed. Thus, for 1,3-butadiene, λ_{max} is 217 mμ and for 2-chloro-1,3-butadiene, λ_{max} is 223 mμ whereas for cyclopentadiene (VIII), λ_{max} is 235 mμ (5)

VIII



IX

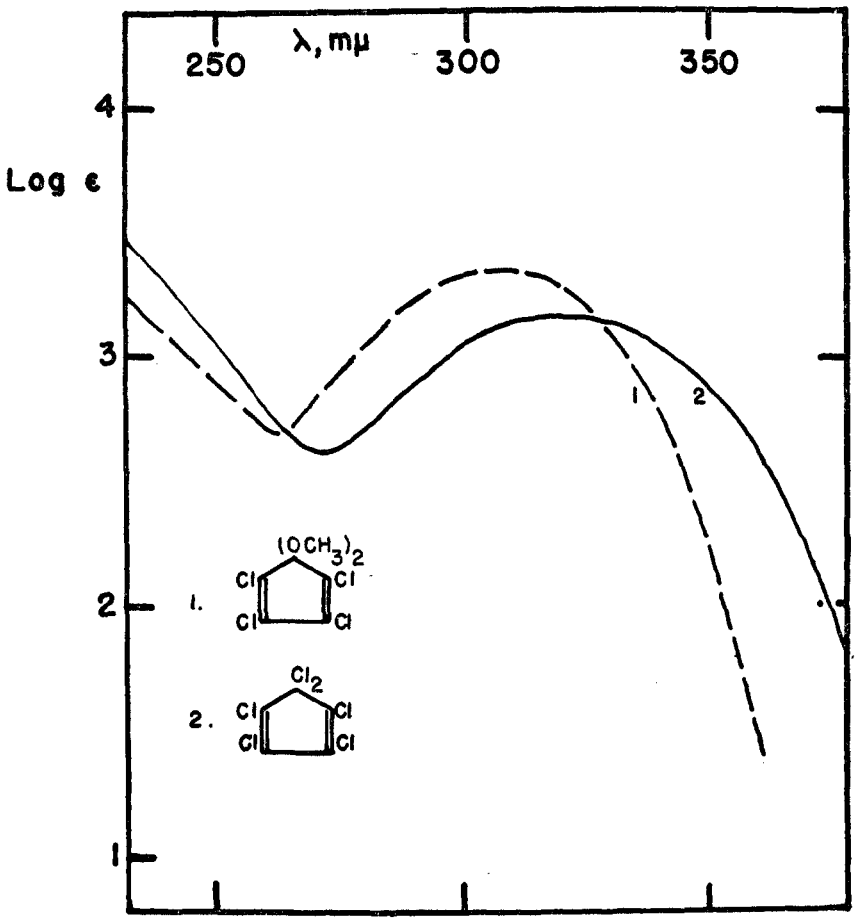
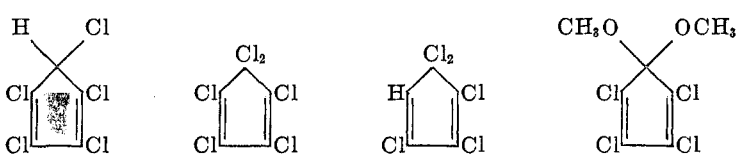


FIG. 4. ULTRAVIOLET SPECTRA IN ETHANOL: ———Hexachlorocyclopentadiene, ——— 5,5-Dimethoxytetrachlorocyclopentadiene.

and for 1,2,3,4-tetrachlorocyclopentadiene (IX); λ_{max} is 276 mμ (Fig. 3).

In contrast with the cyclopentene series, chlorine substitution in the allylic position of cyclopentadiene has a profound effect on the character of absorption. For 1,2,3,4,5-pentachlorocyclopentadiene (X) λ_{max} is 307 mμ and for hexachlorocyclopentadiene (XI), λ_{max} is 322 mμ, indicating red shifts of 31 and 15 mμ for the introduction of the first and second allylic chlorine atoms (Fig. 3). For 2,3,4,5,5-pentachlorocyclopentadiene (6) λ_{max} is 312 mμ (Fig. 3), exactly 10



X XI XII XIII

mμ less than for XI. In addition to the eminent red shift, allylic chlorine substituents in cyclopentadienes also cause a sharp decrease in the absorption intensity. The extent of both the red shift and decrease in intensity appears to depend on the electronegativity of the allylic substituent. For instance when the allylic chlorine atoms of XI are replaced by methoxy groups as in 5,5-dimethoxytetrachlorocyclopentadiene (XIII), (Fig. 4) neither the red shift nor the decrease in absorption intensity is as pronounced as in XI. In this connection it should be noted that the allylic substituent cannot participate directly in resonance with the diene system by mesomeric shift of an electron pair and thus can exert only its inherent negative inductive effect.

EXPERIMENTAL

Measurement of spectra.[2] Ultraviolet spectra were measured in 1-cm. quartz cells with either a Cary recording spectrophotometer or a Beckman Model DU quartz spectrophotometer. The solvent was either 95% ethanol or spectroscopically pure *n*-hexane. Solutions were initially made up as 0.1 *molar* and were diluted appropriately.

Source of compounds. Hexachlorocyclopentadiene was generously supplied by the Hooker Electrochemical Company and was purified by distillation giving a fraction, b.p. 83–84° (3 mm.), n_D^{20} 1.5650. *Octachlorocyclopentene* was obtained from the same source and was recrystallized twice from petroleum ether (b.p. 35–37°) giving colorless plates, m.p. 39–39.5°. Chlorine was added to 1,2,3,4-tetrachlorocyclopentadiene according to Meyers (7) giving *1,2,3,3,5,5-hexachlorocyclopentene*, m.p. after recrystallization from petroleum ether (b.p. 35–37°) 41–42°. Hexachlorocyclopentadiene was reacted with *cis*-dichloroethylene according to Rakoff (8) giving *1,2,3,4,5,6,7,7-octachlorobicyclo[2.2.1]hept-2-ene*, m.p. 170–180° (mixed isomers) after recrystallization from petroleum ether (b.p. 35–37°).

5-Bromomethyl-1,2,3,4-tetrachlorobicyclo[2.2.1]hept-2-ene-7-one was prepared according to McBee, Diveley, and Burch (9), m.p. 108–109° after recrystallization from petroleum ether (b.p. 60–70°). *1,2,3,4,5-Pentachlorocyclopentadiene*, b.p. 81–83° (4 mm.), n_D^{20} 1.5613 after distillation through a Vigreux column and its dimer, *1,2,3,3a,4,5,6,7,7a,8-decachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene*, m.p. 215–216° after recrystallization from petroleum ether (b.p. 35–37°), were prepared starting from hexachlorocyclopentadiene as described by McBee and Smith (10). *Perchloro-3a,4,7,7a-tetrahydro-4,7-methanoindene*, m.p. 221–223° after recrystallization from petroleum ether (b.p. 35–37°) was obtained by chlorination of bis(pentachlorocyclopentadienyl) as described by McBee, Idol, and Roberts (11). *1,2,3,4-Tetrachlorocyclopentadiene*, m.p. 60–61° after recrystallization from petroleum ether (b.p. 35–37°), was prepared by reduction of hexachlorocyclopentadiene with zinc and acid as reported by McBee, Meyers, and Baranauckas (12). *Cyclopentadiene* was obtained by destructive distillation of the dimer. The first distillate was fractionated through a 25-plate metal-packed column. A middle fraction (b.p. 41°) was used for measurement immediately after collection. *5,5-Dimethoxytetrachlorocyclopentadiene*, b.p. 110° (11 mm.), n_D^{20} 1.5284 after rectification through a 12″ glass helices-packed column, was prepared by treating hexachlorocyclopentadiene with sodium hydroxide in methanol according to Newcomer and McBee (13).

SUMMARY

The ultraviolet spectra characteristics of halogen-containing cyclopentenes, cyclopentadienes, and bicyclo[2.2.1]hept-2-enes have been investigated to de-

[2] Acknowledgement is made to Mr. R. Curry and Mr. Wm. Krochta who operated the Cary spectrophotometer.

termine the effect of vinylic and allylic halogen substituents on the λ_{max} and extinction coefficient.

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