Synthesis, Structure, and Configuration of Some Macromolecular Chlorocarbons of High Thermal and Chemical Stability[1]

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Abstract: The syntheses of three macromolecular chlorocarbons [perchloropoly-*p*-xylenediylidene (PP-xynene), $(C_8Cl_6)_m$; perchloropoly-*p*-dipropenylbenzenediylidene (PP-diprobene), $(C_{12}Cl_{10})_m$; and perchloropolybi-*p*-tolyldiylidene (PP-bitylene), $(C_{14}Cl_{10})_m$] starting from perchloro-*p*-xylene, perchloro-1,4-dipropenylbenzenes, and perchlorobi-*p*-tolyl, respectively, are described and their structure and configuration studied. The mechanism of this polycondensation is discussed. These materials have an exceptionally high thermal stability (up to 500°, incipient red heat) and chemical inertness.

As a continuation of our research program in alkaromatic chlorocarbons, it became of interest to investigate the synthesis and properties of macromolecules belonging to this new and unusual class of compounds of which some members have been found to exhibit thermal and chemical stability.[2] Such stability, however, is not necessarily a general feature of the chlorocarbons. Some are known to decompose under relatively mild conditions. For example, perchlorotoluene decomposes at a temperature as low as 185°[3,4] and hydrolyzes easily under acidic conditions.[3] On the other hand, *trans*-perchlorostilbene does not decompose appreciably at 400° and it withstands, with no significant change, strong reagents such as sulfuric or fuming nitric acid.[5]

The reason for the observed reactivity of perchlorotoluene is its high steric strain which greatly assists the fission, both heterolytic and homolytic, of an α-carbon–chlorine bond.[3,6] The unusual stability of *trans*-perchlorostilbene is ascribed to the high carbon (trigonal)–chlorine bond energy. This situation is caused by the high s character of the sp^2 hybridization on the carbon and to resonance involving the lone electron pairs on chlorine.

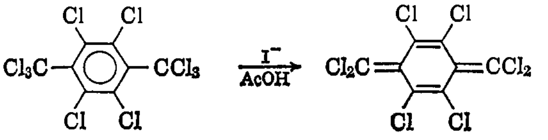
Incorporation of these concepts into macromolecular substances should lead to compounds possessing not only the above-mentioned remarkable stabilities but also other desirable features such as improved physical and mechanical properties. Consequently, it was decided to synthesize polymeric chlorocarbons structurally related to the perchlorostilbenes.

Results and Discussion

A mixture of *cis*- and *trans*-perchlorostilbene (II) is obtained by self-condensation of perchlorotoluene (I) by a dechlorinating agent such as iodide ion in acidic media.[5] Accordingly, the same reaction applied to

$$\underset{\text{I}}{2C_6Cl_5CCl_3} + 4I^- = \underset{\text{II, \textit{cis} and \textit{trans}}}{C_6Cl_5CCl{=}CClC_6Cl_5} + 2I_2 + 4Cl^-$$

perchloro-*p*-xylene (III) might have been expected to yield a macromolecular chlorocarbon. This reaction, however, failed to give any polymeric substance. Instead, an almost quantitative yield of a relatively simple chlorocarbon, the perchloro-*p*-xylylene (or perchloro-*p*-quinodimethan) (IV), was obtained.[7,8]



III IV

Perchloro-*p*-xylylene, unlike all other known *p*-xylylenes, is a remarkably inert substance since it does not polymerize and does not react with oxygen or with some chemically aggressive species.[7]

Fortunately though, other dechlorinating agents, such as stannous chloride and ferrous chloride, have been found to give a good yield of the expected macromolecular material. These reagents have also brought about self-polycondensation of other bis(trichloromethyl)-chlorocarbons, such as perchloro-1,4-dipropenylbenzenes and perchlorobi-*p*-tolyl.

The resulting polymers, as expected, possess an excellent thermal stability and chemical inertness.

A. Perchloropoly-*p*-xylenediylidene[9] **(PP-xynene).**[10] This macromolecular chlorocarbon was synthesized from perchloro-*p*-xylene by reaction with either ferrous chloride or with stannous chloride in dioxane, at 100° and under a nitrogen atmosphere. A good yield

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[1] This research has been sponsored by the Aerospace Research Laboratories, Wright-Patterson Air Force Base, through the European Office of Aerospace Research, under Contract No. AF 61(052)-141.

[2] The absence of hydrogen in the perchlorocarbons might be expected to eliminate one well-known path for reaction or degradation of less highly chlorinated substances: that of elimination of the elements of hydrogen chloride.

[3] M. Ballester, C. Molinet, and J. Castañer, *J. Am. Chem. Soc.*, **82**, 4254 (1960).

[4] M. Ballester, C. Molinet, and J. Rosa, *Anales Real Soc. Espan. Fis. Quim.* (Madrid), **B57**, 393 (1961).

[5] M. Ballester, C. Molinet, and J. Rosa, *Tetrahedron*, **6**, 109 (1959).

[6] M. Ballester and J. Castañer, *J. Am. Chem. Soc.*, **82**, 4259 (1960).

[7] M. Ballester and J. Castañer, *Anales Real Soc. Espan. Fis. Quim.* (Madrid), **B56**, 207 (1960).

[8] M. Ballester and J. Riera, *J. Am. Chem. Soc.*, **86**, 4505 (1964).

[9] The names of the polymeric chlorocarbons here reported derive from the rules recommended by the International Union of Pure and Applied Chemistry (IUPAC), "Handbook for Chemical Society Authors," Special Publication No. 14, The Chemical Society, London, 1960, pp 59, 191.

[10] The authors have been requested by various correspondents to give acronyms to the polymers here described. They have decided to combine within the acronym both initials and a nickname. The initials PP stand for perchloropoly.

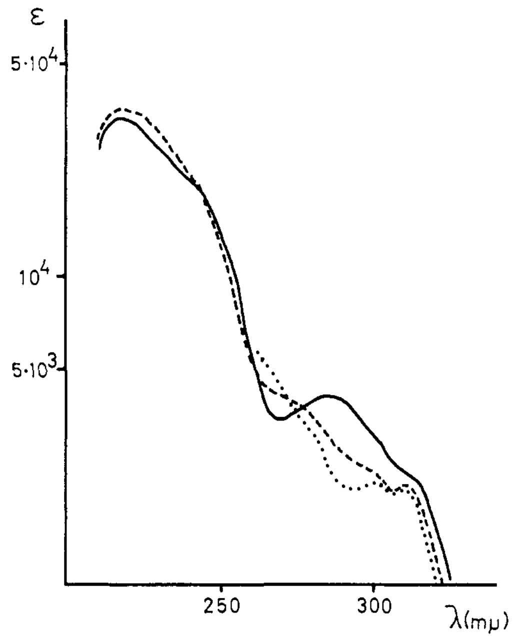


Figure 1. Curve 1, ———, PP-xynene, fractions A and B; curve 2, – – – –, PP-xynene, fraction C; curve 3, ..., heat-treated PP-xynene.

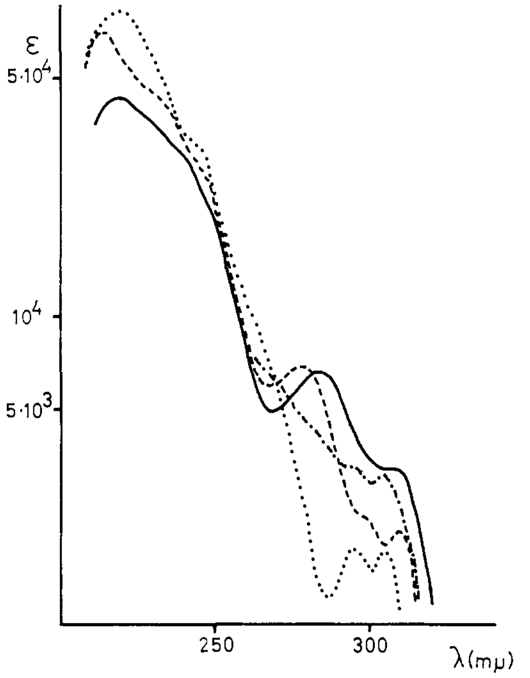


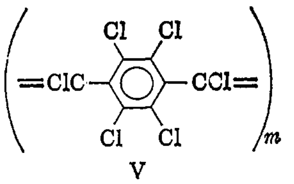
Figure 2. Curve 1, ———, PP-bitylene; curve 2, –·–·–·, ultraviolet- or heat-treated PP-bitylene; curve 3, – – – –, *cis*-perchlorostilbene; curve 4, ..., *trans*-perchlorostilbene.

of an almost white, resinous material of homogeneous chemical composition was obtained. A small amount of perchloro-*p*-xylylene was also isolated.

Three main fractions have been isolated from the reaction product: fraction A, soluble in ethyl ether but insoluble in petroleum ether; fraction B, soluble in chloroform but insoluble in ethyl ether; fraction C, insoluble in chloroform (practically insoluble in all solvents and infusible). In a typical preparation, their relative proportions were 8, 66, and 26%, respectively. Their carbon, hydrogen, and chlorine analyses were consistent with formula $(C_8Cl_6)_m$. The yield was 67–72% of the theoretical value. That for the by-product perchloro-*p*-xylylene was 4–17%.

Vapor pressure osmometry gave, for the two soluble fractions, mean molecular weights around 4000, with the highest values corresponding to the least-soluble fractions. It is likely therefore that the mean molecular weight of fraction C is higher.

The infrared and ultraviolet spectra indicate that the polymeric material has the structure V.



V

Spectra, Structure, and Configuration. The ultraviolet spectra of all fractions have essentially the features of that of a highly chlorinated benzene derivative with conjugating substituents:[11,12] a primary band around 220 mμ, a secondary band around 300 mμ, and a conjugation band between them. For the sake of comparison the absorption curves of fractions A and B, and C (Figure 1, curves 1 and 2) and those of the *cis*- and *trans*-perchlorostilbene (Figure 2, curves 3 and 4) have been plotted.[13]

The spectrum of fractions A and B (Figure 1, curve 1) is similar to that of *cis*-perchlorostilbene (Figure 2, curve 3). It is also noted that the conjugation band in the former is displaced bathochromically with respect to that of the latter, and that it overlaps so much with the secondary band that this latter appears only as a shoulder at 310 mμ.

In fraction C (Figure 1, curve 2) the conjugation band is greatly shifted, both hypsochromically (275 mμ) and hypochromically, with respect to that of fractions A and B (285 mμ) so that more fine-structure features of the secondary band emerge (300 (sh) and 310 (max) mμ).

The pertinent conclusion is that the soluble fractions have high *cis* character, while fraction C has a significantly greater *trans* character.

The bathochromic shift with respect to the *cis*-perchlorostilbene is accounted for in terms of increased resonance, since two conjugating vinylene groups per benzene nucleus are present here instead of one.

The maximum absorptivity for the secondary band of the "monomeric fragment" $=CClC_6Cl_4CCl=$ can easily be calculated by means of Ballester–Riera–Spialter spectral law based on the theory of the migration (spectroscopic) moment of the substituents.[11] Since the moments for constellations 1,3,2-Cl_2(*cis*-CCl=CClC$_6$Cl$_5$) and 1,3,2-Cl_2(*trans*-CCl=CClC$_6$Cl$_5$) are, respectively, 32.5 and 29, the resultant moment should be twice as high, *i.e.*, 65 and 58, respectively. These values correspond to maximum molar absorptivities of

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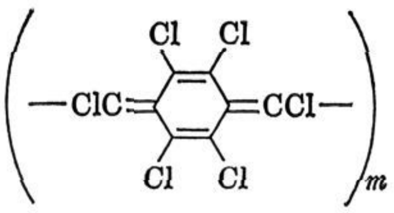
(11) M. Ballester, J. Riera, and L. Spialter, *J. Am. Chem. Soc.*, **86**, 4276 (1964).

(12) M. Ballester, *et al.*, *Anales Real Soc. Espan. Fis. Quim.* (Madrid), **B56**, 197, 203, 723 (1960); M. Ballester, J. Palau, and J. Riera, *J. Quant. Spectr. Radiative Transfer*, **4**, 819 (1964).

(13) Conjugation band: *cis*-perchlorostilbene, λ 279 (max) mμ; *trans*-perchlorostilbene, λ 260 (sh) mμ. Secondary band: *cis*-perchlorostilbene, λ 299 (sh), 310 (max) mμ; *trans*-perchlorostilbene, λ 295 (max), 306 (max) mμ.

2350 (*cis*) and 2070 (*trans*), which are, within the error of measurement, equal to the experimental values (ϵ 2000–2300). Since the difference between the calculated values is not high, no conclusion can be drawn on this basis with respect to the degree of *cis* or *trans* character in these fractions.

There was the possibility that the macromolecular chlorocarbon had the quinoid structure VI. This is unlikely since, as a result of the great steric interactions among the α substituents and the *ortho* chlorines, the "*exo*" double bonds would be highly twisted. Furthermore, as we have seen, the ultraviolet spectrum is quite consistent with the benzenoid structure V.


VI

The most dramatic proof ruling out structure VI is afforded by the infrared spectrum (Figure 3). Observation of the spectra of hundreds of highly chlorinated and perchlorinated benzenes has allowed us to conclude that the very strong "stretching" benzenoid peak group is located around 7.5 μ (1350 cm^{-1}).[14] In the polymeric fractions, such a group is indeed found there. Another fact is the absence of the intense ethylene "stretching" peaks found in perchloro-*p*-xylylene to be expected if the structure were VI.[14] Notice also the presence of a weak peak at 1540 cm^{-1}. This indicates the lack of a center of symmetry in the benzene ring,[14] and therefore it is a further indication of significant *cis* character. In the same connection, it is necessary to mention that the high-concentration spectrum of fractions A and B reveals clearly a weak peak at 1597 cm^{-1} and a shoulder at 1610 cm^{-1}. These are "stretching" frequencies for the perchlorinated ethylene bond. Comparison with the data on the perchloropropenylbenzenes[14] indicates that these two peaks are presumably associated with *trans* (unsymmetrical) and *cis* character, respectively.[15] These observations are in full agreement with the ultraviolet data.

Correlation with the ultraviolet data leads to the conclusion that the *cis* character is associated with peaks at 1280 (w) and 780 (m) cm^{-1}, while the *trans* character is in turn related to peak at 835 cm^{-1} (Figure 3).[16] Accordingly, in fraction C (Figure 3, curve 2), which has a greater *trans* character, the two former peaks are weaker, while the latter is significantly stronger than in fractions A and B (Figure 3, curve 1).

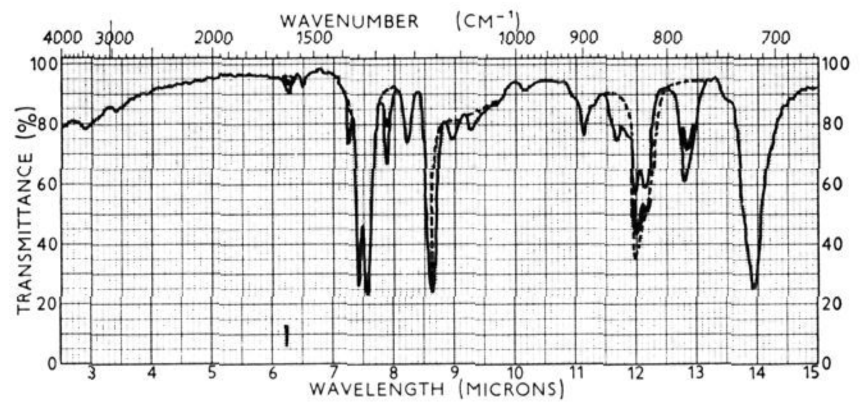


Figure 3. Continuous line, PP-xynene; broken line, heat-treated PP-xynene; thick line, ultraviolet-treated PP-xynene.

The above conclusions are substantiated further with the results of treating the polymer with ultraviolet light or by heat. It is known that ultraviolet light converts the *cis*-perchlorostilbene into its *trans* isomer.[5,17] Accordingly, it has been found that, under the same conditions, a product is obtained from fraction B (or A), the spectrum of which shows a much weaker conjugation band, being indistinguishable from that of fraction C (Figure 1, curve 2). Part of the product is insoluble in carbon tetrachloride. This supports further the idea that *trans* character is a cause for a diminished solubility.[18] The intensity changes in the infrared spectrum show also a greater *trans* character, since its absorption is indistinguishable from that of fraction C (Figure 3, curve 2).

Heating fraction C at 450–500° results in a product which analyzes well, the infrared spectrum of which shows a complete lack of peaks attributed to the *cis* character (1280 and 780 cm^{-1}) and a great enhancement of the peak at 835 cm^{-1} (Figure 3, curve 3). Also, the very strong peak at 1160 cm^{-1} is found now at 1170 cm^{-1} and is much sharper. This is most probably due to disappearance of a very strong peak at 1160 cm^{-1} associated with *cis* character. These results support the conclusion that *cis*-to-*trans* stereomutation is here complete. Accordingly, the ultraviolet spectrum (Figure 1, curve 3) shows the weakest conjugation band and, consequently, the fine structure of the secondary band is as well defined as that of the *trans*-perchlorostilbene (two maxima; Figure 2, curve 4).

The thermal stability of this macromolecular chlorocarbon is remarkable. Fraction C withstands *in vacuo* temperatures up to 500° for at least 1 hr, without significant decomposition, as ascertained by weight loss and elemental analysis. Thermal stability appears to

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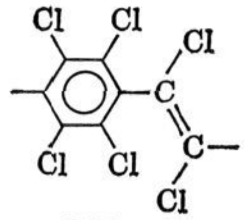
(14) M. Ballester, J. Castaner, and J. Riera, unpublished correlations.

(15) In highly chlorinated and perchlorinated benzene derivatives, the so-called "stretching" peaks are significantly shifted bathochromically. The main benzenoid group, which is commonly located around 1500 cm^{-1}, is here found at about 1350 cm^{-1}. The ethylene peak, normally found around 1650 cm^{-1}, is noted around 1600 cm^{-1}. This general shift is accounted for in terms of resonance involving the chlorine lone electron pairs which diminish the strength to the carbon–carbon bond.[14] The higher "stretching" frequency of the *cis* configuration in the perchloropropenylbenzenes (*cis*, 1610 cm^{-1}; *trans*, 1597 cm^{-1}) can be attributed to a greater steric inhibition of resonance between the perchlorovinylene group and the benzene nucleus. Steric interaction takes place between the *ortho* chlorines and the substituent on the β-ethylene carbon. In the *trans* isomer the latter substituent is a chlorine, but in the *cis* isomer it is a much bulkier trichloromethyl group, and, consequently, resonance is then more inhibited. From this and other comparable situations, it is concluded that the borderline frequency between both configurations is 1605 cm^{-1}.[14]

(16) In fact, the peak at 835 cm^{-1} seems to be present in all substances with grouping VII, *i.e.*, with the *trans* configuration.[14] In this connection it is pointed out that this peak is present in *trans*-perchlorostilbene but is absent in its *cis* isomer.


VII

(17) M. Ballester and J. Rosa, *Tetrahedron*, **9**, 156 (1960).

(18) The solubility of *trans*-perchlorostilbene is extremely low. In ethyl ether or benzene the *trans* isomer is, respectively, $^{1}/_{100}$ and $^{1}/_{400}$ as soluble as its *cis* isomer.[17]

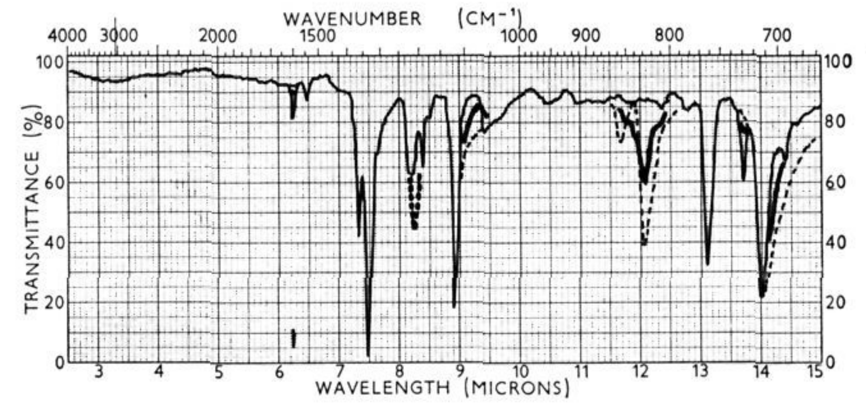


Figure 4. Continuous line, PP-bitylene; broken line, heat-treated PP-bitylene; thick line, ultraviolet-treated PP-bitylene.

be associated with *trans* character. As expected from this observation, ultraviolet irradiation, which causes *cis*-to-*trans* conversion, seems to improve the stability of the polymer.

Good chemical inertness to strong acids and bases was also noted.

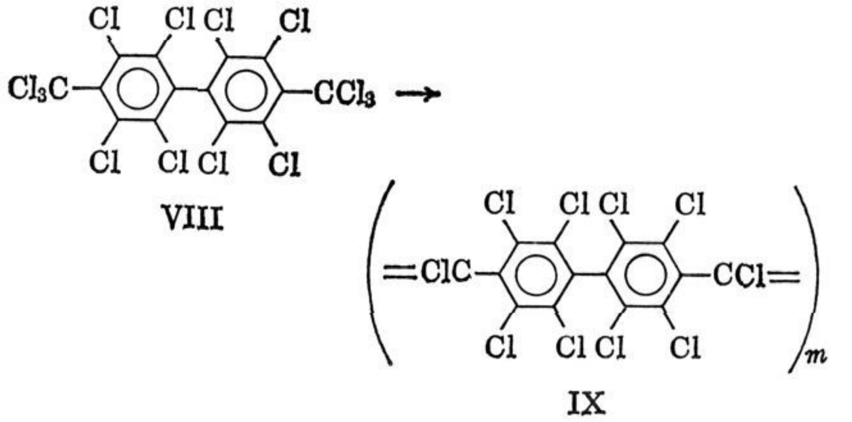
B. Perchloropolybi-*p*-tolyldiylidene (PP-bitylene). This macromolecular chlorocarbon was synthesized from perchlorobi-*p*-tolyl by the reaction with stannous chloride in dioxane at 100° and under nitrogen.

Treatment of the product with ethyl ether gives two main fractions. The soluble fraction was discarded since it had a substantial amount of aliphatic hydrogen and carbonyl group content (determined from the infrared spectrum). The fraction insoluble in ether yielded the macromolecular chlorocarbon as a white, infusible powder, soluble in carbon tetrachloride.

The carbon, hydrogen, and chlorine analyses agreed with the formula $(C_{14}Cl_{10})_m$. The yield was 67% of the theoretical.

Vapor pressure osmometry of subfractions obtained by fractional precipitation gave mean molecular weight values ranging from 5000 to 27,000, as solubility decreased.

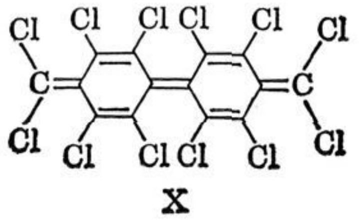
Both ultraviolet and infrared spectra are consistent with structure IX.



VIII

IX

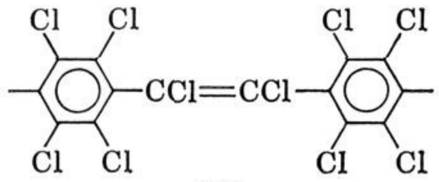
Because of the extensive twisting of the central bond caused by steric interaction among the *ortho* chlorines, it was unlikely that the quinoid structure X, the analog of structure IV, could result. In fact, polycondensation with iodide ion in acetic acid is here possible, although there is extensive solvolysis of terminal trichloromethyl groups.



X

Spectra, Structure, and Configuration.[19] The ultraviolet absorption spectrum of the polymer is depicted in Figure 2, curve 1. Like other highly chlorinated benzene derivatives with conjugating substituents,[11,12] it has a primary band around 220 mμ, with a shoulder at 245 mμ, a conjugation band around 285 mμ, and a secondary band appearing as a shoulder at 310 mμ. For purposes of comparison, the spectra of the perchlorostilbenes have been included in Figure 2 (curves 3 and 4).[13] Curve 1 is very similar to curve 3 (*cis*-perchlorostilbene). Consequently, it is concluded that PP-bitylene has a high *cis* character.

It should be mentioned that the very intense "biphenyl" conjugation band is not present[20] because steric inhibition of resonance due to interaction among chlorines makes the joined benzene rings spectroscopically independent.[21] This is why the spectrum of the polymer is so close to that of *cis*-perchlorostilbene. The chromophoric unit of PP-bitylene is therefore XI.



XI

It is possible to calculate an approximate value for the maximum molar absorptivity of the secondary band of PP-bitylene. Since the moment of constellations 1,3,2-$Cl_2(C_6Cl_4R)$ and 1,3,2-$Cl_2(CCl{=}CClC_6Cl_5)$ are approximately 20[21] and 30,[11] respectively, the moment for the structural unit $=CClC_6Cl_4-$ should be about 50. This value corresponds to a calculated absorptivity of 3500 units for that chromophoric unit, 200 units greater than the experimental value (3300), and well within experimental error.

The infrared spectrum of PP-bitylene (Figure 4, curve 1) shows the expected very intense benzenoid peak group at 7.5 μ (1350 cm^{-1}), a very weak peak at 1600 cm^{-1} due to ethylene "stretching," and another one at 1540 cm^{-1} (first benzenoid peak). All these maxima are also present in PP-xynene.

The presence of a peak at 1540 cm^{-1} is consistent with the lack of center of symmetry in *both cis* and *trans* configurations.

It is to be noted also that there is no *trans* structure peak at 835 cm^{-1}. However, by irradiation with ultraviolet light or by heating above 450°, absorption appears at 830 cm^{-1} while, as expected, that at 1600 cm^{-1} becomes extremely weak (Figure 4, curves 2 and 3).

The ultraviolet spectrum of the ultraviolet- or heat-treated polymer (Figure 2, curve 2) shows a much less strong conjugation band and, consequently, the fine structure of the secondary band becomes apparent (a shoulder at 295 and a maximum at 305 mμ).

These spectral changes are attributed to *cis*-to-*trans* stereomutation which, as in PP-xynene, are more extensive when they are caused by heat treatment (Figure 4, curve 3). As in PP-xynene also, solubility diminishes with increasing *trans* character and molecular weight.

The thermal stability of PP-bitylene is very high. A sample heated in the air at 500° (incipient red heat) for

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(19) For full discussion of some effects, see PP-xynene.

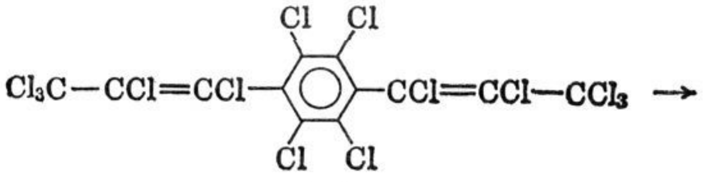
(20) The "biphenyl" conjugation band in 4,4′-bistrichloromethylbiphenyl is characterized by an intense maximum (ε 30,000) at 270 mμ.[14]

(21) M. Ballester and J. Riera, unpublished.

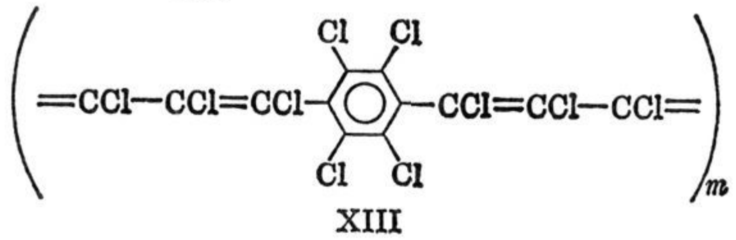
5 min showed no significant decomposition, as ascertained by weight loss and elemental analyses.

C. Perchloropoly-*p*-dipropenylbenzenediylidene (PP-diprobene). This macromolecular chlorocarbon was obtained from either perchloro-*p*-dipropenylbenzene, mp 184° (XII), or from its isomer, mp 281° (XII), by the reaction with stannous chloride in dioxane containing some chloroform at 100° and under nitrogen. The carbon, hydrogen, and chlorine analyses were consistent with the formula $(C_{12}Cl_{10})_m$. The yields were excellent (about 90% of the theoretical). The molecular weights ranged from 15,000 to 20,000.

The spectra are interpreted as indicating the structure XIII.



XII



XIII

Spectra, Structure, and Configuration.[19] The ultraviolet spectrum showed a smoothly decreasing absorption from 260 to 340 mμ. However, two slight shoulders at 285 and 315 mμ could still be noticed. They correspond, presumably, to the conjugation band, stronger than in the preceding polymers, and the secondary band, respectively. The latter band is also more intense than in PP-xynene. This is probably due to strong overlap with the conjugation band. Also, this indicates strong *cis* character for the vinylene groups attached directly to the benzene nuclei.

The infrared spectrum (Figure 5) shows a relatively broad, weak peak at 1620 cm^{-1} and a very weak peak at 1580 cm^{-1}, both due to ethylene "stretching." The weak peak at 1545 cm^{-1} is the first benzenoid "stretching." The very intense peak group around 1350 cm^{-1}, characteristic of the highly chlorinated benzenes, is also found.

The spectrum of PP-diprobene does not undergo any significant change after illumination with ultraviolet light, or by heating in the air at 400° for a short period. However, with the latter treatment part of the product becomes insoluble in carbon tetrachloride.

D. The Mechanism. It has been shown that the condensation of perchlorotoluene by iodide ion in acetic acid to give the perchlorostilbenes occurs through the perchlorobenzyl radical.[5] Since solvolysis of perchlorotoluene takes place at a comparable rate, this radical is probably preceded by the formation of perchlorophenylcarbonium ion. Presumably, a carbonium ion is also formed in the reaction of perchloro-*p*-xylene with iodide ion to give the observed quantitative yield of perchloro-*p*-xylylene.[7]

In the dechlorination with stannous chloride a monoradical is formed directly,[22] which dimerizes or loses again a second chlorine.

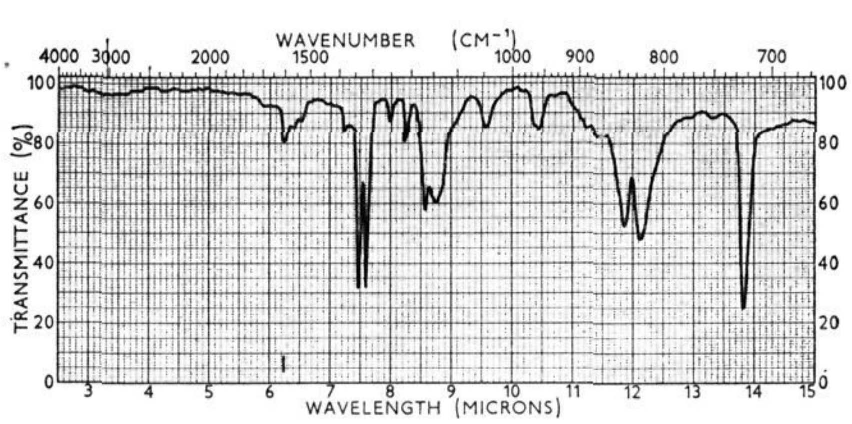
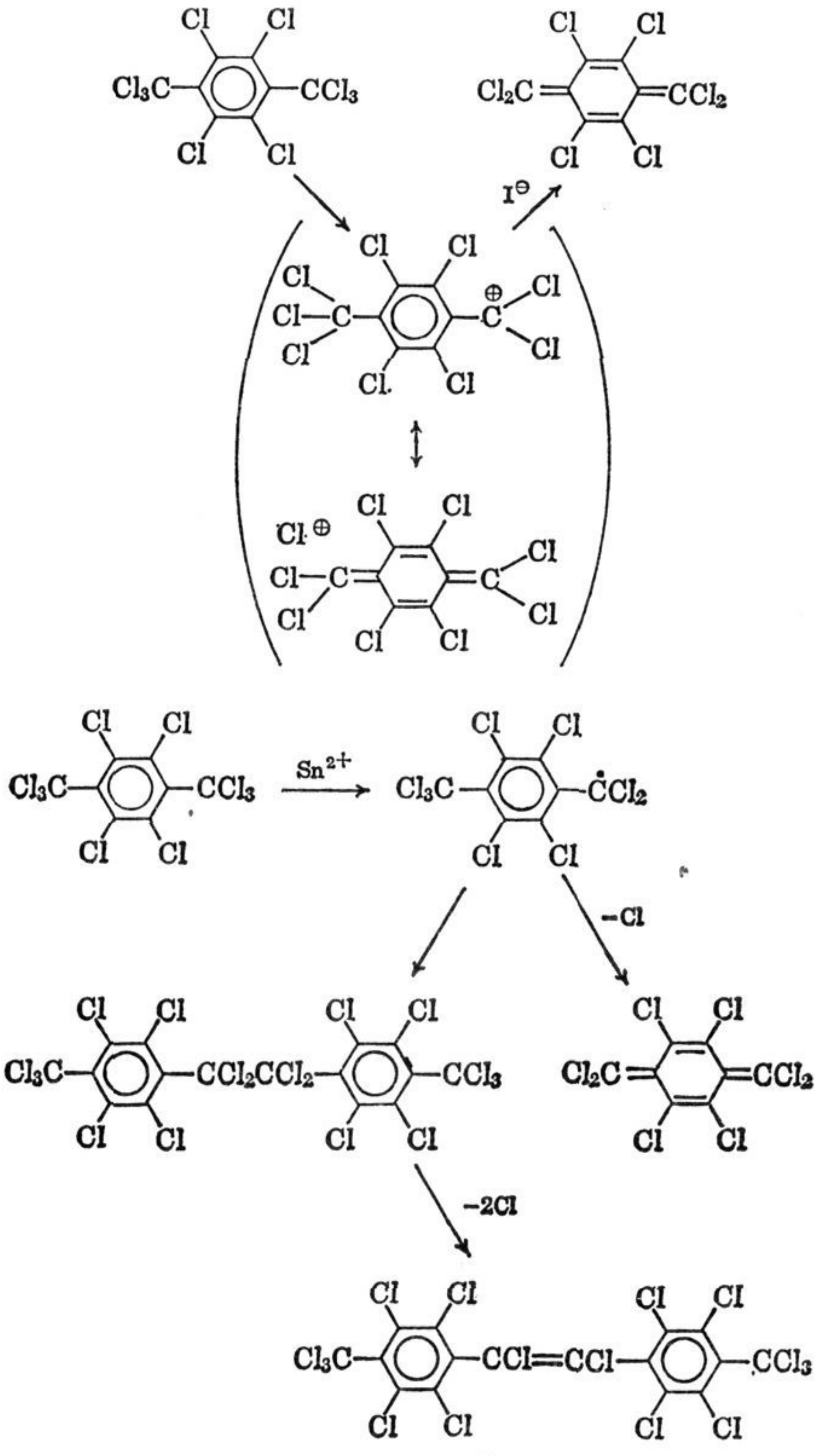


Figure 5. PP-diprobene.

Dechlorination to stilbene is here greatly assisted by the high steric strain in its bibenzyl precursor, as in the case of perchlorotoluene.[5] In this connection it is mentioned that the latter condensation can be carried out by stannous chloride, giving *trans*-perchlorostilbene, *cis*-perchlorostilbene, αH-heptachlorotoluene, and perchlorobenzoyl chloride (yields 49, 40, 4, and 0.5%, respectively).[21]



(*cis* and *trans*)

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[22] In fact, in the reaction of perchlorodiphenylmethane with stannous chloride, perchlorodiphenylmethyl (PDM), a stable free radical, is formed.[8]

The dechlorination process, with formation of monoradicals of increasing size, continues on to give the macromolecular chlorocarbon.

The formation of intermediate biradicals in this polymerization seems not to be extensive. Evidence for this comes from the observed relatively low yield of perchloro-*p*-xylylene, which is expected to be the most favorable case for a secondary attack upon a monoradical by the dechlorinating species.

A polymerization mechanism involving radical addition to the perchloro-*p*-xylylene is unlikely since this chlorocarbon is a remarkably inert substance.[7] Furthermore, the addition intermediates should possess high steric strain and, consequently, their formation should be hindered.[3]

In the opinion of the authors, the general mechanism for any polycondensation of a bistrichloromethyl aromatic substance of the type here described can be summarized as follows.

$$\begin{gathered}
\mathrm{Cl_3C(CCl{=}CCl)}_p\mathrm{[Ar(CCl{=}CCl)}_{2p+1}]_m\mathrm{Ar(CCl{=}CCl)}_p\mathrm{CCl_3} \\
\Big\downarrow \mathrm{Sn^{2+}} \\
\mathrm{Cl_3C(CCl{=}CCl)}_p\mathrm{[Ar(CCl{=}CCl)}_{2p+1}]_m\mathrm{Ar(CCl{=}CCl)}_p\mathrm{\dot{C}Cl_2} \\[1ex]
\mathrm{Cl_3C(CCl{=}CCl)}_p\mathrm{[Ar(CCl{=}CCl)}_{2p+1}]_m\mathrm{Ar(CCl{=}CCl)}_p\mathrm{\dot{C}Cl_2} \\
+ \\
\mathrm{Cl_3C(CCl{=}CCl)}_p\mathrm{[Ar(CCl{=}CCl)}_{2p+1}]_n\mathrm{Ar(CCl{=}CCl)}_p\mathrm{\dot{C}Cl_2} \\
\Big\downarrow \\
\mathrm{Cl_3C(CCl{=}CCl)}_p\mathrm{[Ar(CCl{=}CCl)}_{2p+1}]_{m+n+1}\mathrm{Ar(CCl{=}CCl)}_p\mathrm{CCl_3}
\end{gathered}$$

In the cases studied here, for Ar = C_6Cl_4, $p = 0$, 1; for Ar = $C_6Cl_4C_6Cl_4$, $p = 0$; for the starting materials, $m = 0$.

Experimental Section

Spectra. The ultraviolet spectra were taken with a Hilger "Uvispek" Model H-700 spectrophotometer. Solvents used were purified cyclohexane and carbon tetrachloride.

The infrared spectra were determined with Perkin-Elmer "Infracord" Models 137 and 137G. The media were purified carbon disulfide and tetrachloroethylene, or potassium bromide (pellet).

Osmometry. The molecular weight data have been obtained with a Mechrolab Model 301A vapor pressure osmometer. Purified chloroform was used as the solvent.

Preparation of Perchloropoly-*p*-xylenediylidene (PP-xynene) with Stannous Chloride. A mixture containing 7.00 g of perchloro-*p*-xylene, 10.6 g of stannous chloride dihydrate,[23] 350 g of purified dioxane, and 17.5 g of chloroform[24] was refluxed under purified nitrogen for 5 hr. The reaction mixture was poured into 1.5 l. of diluted aqueous hydrochloric acid, and the resulting mass was filtered, washed, and dried. The collected light powder (5.51 g) was digested with 200 ml of refluxing ethyl ether and filtered, when cold, giving a residue (3.70 g) and an **extract A_1** (1.68 g). The residue was digested in boiling chloroform and filtered at room temperature, leaving 1.02 g of **residue C**. The fraction soluble in chloroform (2.53 g) was purified by passing its carbon tetrachloride solution through activated alumina. This solute, after an ether wash,[25] gave **fraction B**, weighing 2.17 g.

Fraction A_1 was dissolved in carbon tetrachloride and passed through activated alumina. The solute (1.26 g) was digested with 100 ml of boiling petroleum ether and filtered when cold. The insoluble portion, **fraction A**, weighed 0.30 g. The extract (0.96 g), by fractional sublimation under 0.01 mm pressure, gave 0.23 g of pure perchloro-*p*-xylylene, which was identified by its infrared spectrum, melting point, and mixture melting point. The residue (0.73 g) was impure polymer containing significant amounts of aliphatic hydrogen (infrared spectrum and analyses).

Anal.[26] Calcd for C_8Cl_6: C, 31.1; H, 0.0; Cl, 68.9. Found for A: C, 30.8; H, 0.6; Cl, 68.7. Found for B: C, 30.8; H, 0.4; Cl, 68.6; mol wt, 4200. Found for C: C, 30.4; H, 0.5; Cl, 68.5.

The combined yield of fractions A, B, and C was 72%; yield of perchloro-*p*-xylylene, 3.9 %; over-all yield, 75.9%. The solubility of fraction C (CCl_4, room temperature) was 0.01 g/100 ml.

The ultraviolet spectra (calcd for C_8Cl_6) of fractions A and B (Figure 1, curve 1) showed λ 270 (min), 280–285 (max), 310 (sh) mμ (ε 3700, 4000, 2200); fraction C (Figure 1, curve 2) λ 275 (sh), 300 (sh), 305 (min), 309 (max) mμ (ε 2500, 1450, 1300, 1320). The molar absorptivities for fraction C were minimal values since this fraction was extremely insoluble.

The infrared spectrum of fraction A (Figure 3, curve 1) showed ν 1600 (vw), 1540 (vw), 1380 (w), 1350 (vs), 1325 (vs), 1270 (w), 1220 (w), 1160 (vs), 1120 (vw), 1085 (vw), 990 (vw), 900 (w), 860 (w), 835 (m), 825 (m), 780 (m), 720 (vs) cm^{-1}. Fraction B (Figure 3, curve 2) was similar to fraction A, except that the intensities of the peaks at 835 and 780 became strong and weak, respectively. Also, at high concentrations with the Infracord 137G, the peak at 1600 cm^{-1} was resolved into two peaks at 1595 and 1610 cm^{-1}. The spectrum of fraction C was identical with that of fraction B.

Preparation of Perchloropoly-*p*-xylenediylidene (PP-xynene) with Ferrous Chloride. A mixture containing 12.4 g of perchloro-*p*-xylene, 35.0 g of ferrous chloride dihydrate, 190 g of purified dioxane, and 63.5 g of water was stirred and refluxed under nitrogen for 24 hr. The resulting mixture was poured into water, acidified with hydrochloric acid, treated with ethyl ether, and filtered.

The ethereal layer of the two-layer filtrate contained a brown solute (2.63 g). This was dissolved in chloroform and passed through activated alumina to give a yellowish solid mixture (2.41 g) which by treatment with petroleum ether and sublimation at 0.01 mm yielded 1.87 g of perchloro-*p*-xylylene and 0.21 g of **fraction A** melting at 320–330°. (Other small fractions were obtained the analyses of which were close (within 1%) of that of C_8Cl_6, and with absorption spectra very similar to those of fraction A.)

The fraction insoluble in ethyl ether was digested in hot chloroform and then left at room temperature for several hours. The solid was separated by centrifugation. It was then redigested in chloroform, and the operation was repeated a few times, leaving finally a small (0.69 g) insoluble **residue C**. In this process, **fractions B_1, B_2,** and **B_3**, weighing, respectively, 5.00, 0.51, and 0.34 g, were obtained.

Anal. Calcd for C_8Cl_6: C, 31.1; H, 0.0; Cl, 68.9. Found for A: C, 31.1; H, 0.5; Cl, 68.2. Found for B_1: C, 30.9; H, 0.4; Cl, 69.0; mol wt, 3350. Found for B_2: C, 31.0; H, 0.6. Fractions B_3 and C gave values about 1% off.

Fractions A, B_1, and B_2 combined represent a yield of 67.3%. Since that of perchloro-*p*-xylylene is 17.7%, the over-all yield is 85%.

The solubility (CCl_4, room temperature) of fraction B_3 was 0.1 g/100 ml; that for fraction C, 0.01 g/100 ml.

The ultraviolet spectra of fractions A, B_1, and B_2 were identical with that of fraction A in the preceding polymerization. Those of fractions B_3 and C were similar but the absorption around 280 mμ was weaker, causing the curve from 270 to 310 mμ to be almost a straight slope. Because of insolubility the molar absorptivities were not accurate.

The infrared (Figure 3, curve 1) spectrum of fraction B_1 was similar to fraction B of the preceding preparation, except that the peak at 1380 cm^{-1} (w) was not found here and a new peak at 1780 (w), probably carbonyl "stretching," was present. The remaining fractions had spectra like those of the corresponding fractions in the previous preparation, with the addition of a very weak to weak peak at 1780 cm^{-1}.

Effect of Ultraviolet Light upon PP-xynene. A solution of 0.153 g of fraction B (stannous chloride preparation) in 20 ml of dry, purified carbon tetrachloride was illuminated in a quartz vessel during 24 hr with a 500-w mercury lamp located at a distance of 5 cm. The insoluble material formed (B_i, 0.085 g) was collected, washed, and dried. The mother solution was passed through activated alumina and yielded more material (B_s, 0.060 g).

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(23) Anhydrous stannous chloride gives a very dark product. The appearance of the material improves dramatically when the dihydrate is used instead.

(24) Preliminary experiments seemed to indicate that polycondensation in the presence of chloroform improves the properties of the product by probably favoring the formation of more stable terminal groups.

(25) Fraction B gives with carbon tetrachloride a very stable solvate which does not decompose appreciably at 190° under vacuum (0.01 mm). However, the solvent can easily be eliminated by washing the powdered solvate with ethyl ether.

(26) The usual combustion techniques for carbon–hydrogen analysis give rather high hydrogen values when analyzing certain chlorocarbons.

Anal. Calcd for C_8Cl_6: C, 31.1; H, 0.0; Cl, 68.9. Found for B_i: C, 31.1; H, 0.4; Cl, 68.7. Found for B_s: Cl, 69.0; mol wt, 4000.

The solubility (CCl_4, room temperature) of B_i was 0.01 g/100 ml.

The ultraviolet spectra of fractions B_s and B_i were, within the limits of experimental error, identical with those of fractions A (or B) and C, respectively (Figure 1, curves 1 and 2).

The spectral effect occurring upon irradiation of fraction A was in the same direction as for B, but to a smaller extent.

Spectral Effects upon Heating PP-xynene. A sample of C was heated at 500° under vacuum for 5 min.

Anal. Calcd for C_8Cl_6: C, 31.1; H, 0.0. Found: C, 30.9; H, 0.1.

Because of low solubility of the product, only the wavelength of the important spectral features in the ultraviolet spectrum could be ascertained with accuracy (Figue 1, curve 3): λ 293 (min), 300 (max), 305 (min), 310 (max) mμ.

Preparation of Perchloropolybi-*p*-tolylidiylidene (PP-bitylene). A mixture of 5.00 g of perchlorobi-*p*-tolyl, 5.20 g of stannous chloride dihydrate, and 120 g of purified dioxane was refluxed under purified nitrogen for 4 hr. The mixture was then poured into dilute aqueous hydrochloric acid and the bulky precipitate formed was collected by filtration. After a water wash and drying at 180°, under 0.1 mm pressure, it appeared as a yellowish powder (3.97 g). It was digested with boiling ethyl ether, and the soluble part (0.66 g) was discarded since it had much aliphatic hydrogen and carbonyl groups (infrared spectrum). The insoluble fraction (3.24 g), after passage through activated alumina in carbon tetrachloride, was fractionated by precipitation with petroleum ether. Four fractions were obtained: F_1, F_2, F_3, and F_4 weighing, respectively, 0.28, 1.46, 0.83, and 0.61 g.[27]

Anal. Calcd for $C_{14}Cl_{10}$: C, 32.2; H, 0.0; Cl, 67.8. Found for F_2: C, 32.2; H, 0.1; Cl, 68.0; mol wt, 11,700. Found for F_3: C, 32.3; H, 0.2; Cl, 68.1; mol wt, 8100. Found for F_4: C, 31.9; H, 0.2; Cl, 67.8; mol wt, 5000. Found for F_1: mol wt, 27,000. Fraction F_1 gave values about 1% off.

The total yield of fractions F_2, F_3, and F_4 was 74%.

All fractions (calcd for $C_{14}Cl_{10}$) had identical ultraviolet spectrum (Figure 2, curve 1): λ 218 (max), 245 (sh), 268 (min), 277 (sh), 284 (max), 307 (sh) mμ; ϵ 55,000, 30,000, 5400, 6300, 7100, 3300.

All fractions had the same infrared spectrum (Figure 4, curve 1): ν 1600 (w), 1540 (w), 1365 (m), 1335 (vs), 1215 (w), 1185 (w), 1120 (s), 1050 (w), 760 (s), 728 (w), 712 (s) cm^{-1}.

Effect of Ultraviolet Light upon PP-bitylene. In a quartz vessel, a solution of 0.204 g of polymer dissolved in 8 ml of purified carbon tetrachloride was illuminated for 48 hr, under nitrogen, with a 500-w mercury lamp situated at distance of 7.5 cm. The resulting solution was filtered through activated alumina and the solvent was eliminated as usual. A small amount (0.007 g) of material soluble in ethyl ether was separated. The product weighed 0.193 g.

Anal. Calcd for $C_{14}Cl_{10}$: C, 32.2; H, 0.0; Cl, 67.8. Found: C, 32.4; H, 0.2; Cl, 67.8.

The ultraviolet spectrum (Figure 2, curve 2) showed λ 295 (sh), 301 (min), 305.5 (max) mμ; ϵ 3100, 2800, 3000.

The infrared (Figure 4, curve 2) spectrum was similar to that of the starting material. The peak at 1600 cm^{-1} was weaker; the peak at 1220 cm^{-1} was stronger; the peak at 728 cm^{-1} disappeared; a medium strong peak at 830 and a weak peak at 850 cm^{-1} appeared.

Spectral Effect upon Heating PP-bitylene. Fractions F_2 and F_4 were heated in the air during 5 min at 500°.

Anal. Calcd for $C_{14}Cl_{10}$: C, 32.2; H, 0.0; Cl, 67.8. Found for F_2: C, 31.9; H, 0.2; Cl, 67.8. Found for F_4: C, 32.6; H, 0.1; Cl, 67.6.

Part of the product was insoluble in carbon tetrachloride. The ultraviolet spectrum is very similar to that of the starting polymer. However, the infrared spectrum showed the same changes as in the ultraviolet-treated polymer but, here, they were more pronounced (Figure 4, curve 3).

Preparation of Perchloropoly-*p*-dipropenylbenzenediylidene (PP-diprobene) from Perchloro-*p*-dipropenylbenzene (mp 281°). A mixture consisting of 1.00 g of perchloro-*p*-dipropenylbenzene (mp 281°), 1.36 g of stannous chloride dihydrate, 2.5 g of chloroform, and 75 g of purified anhydrous dioxane was heated at 100° under nitrogen for 6 hr. The reaction mass was poured into dilute aqueous hydrochloric acid and the precipitate formed was collected by filtration, washed, and dried, and then treated with ethyl ether. The fraction soluble in ether (0.033 g) contained much aliphatic hydrogen and carbonyl group and, consequently, was discarded. The insoluble part (0.804 g) was dissolved in carbon tetrachloride and passed through activated alumina. After elimination of the solvent, the residue was thoroughly washed with ethyl ether (to eliminate the carbon tetrachloride). The almost white product obtained weighed 0.704 g, 90% yield.

Anal. Calcd for $C_{12}Cl_{10}$: C, 28.9; H, 0.0; Cl, 71.1. Found: C, 28.8; H, 0.3; Cl, 71.0; mol wt, 15,000.

The ultraviolet spectrum showed λ 285 (sh), 315 (sh) mμ; ϵ 8000, 3700. Since it was determined in carbon tetrachloride solution, only the range 260–360 mμ was measured.

The infrared spectrum showed (Figure 5) ν 1620 (w), 1580 (vw), 1545 (vw), 1400 (vw), 1350 (vs), 1330 (vs), 1255 (vw), 1220 (w), 1170 (m), 1150 (m), 1050 (w), 845 (m), 825 (s), 725 (vs) cm^{-1}.

Preparation of Perchloropoly-*p*-dipropenylbenzenediylidene (PP-diprobene) from Perchloro-*p*-dipropenylbenzene (mp 184°). A mixture of 0.523 g of perchloro-*p*-dipropenylbenzene (mp 184°), 0.70 g of stannous chloride dihydrate, 1.25 g of chloroform, and 40 g of purified anhydrous dioxane was refluxed under nitrogen during 6 hr. The reaction mass was treated as in the preceding preparation. The resulting insoluble part consisted of 0.359 g of an almost white powder, 91% yield.

Anal. Calcd for $C_{12}Cl_{10}$: C, 28.9; H, 0.0; Cl, 71.1. Found: C, 29.1; H, 0.3; Cl, 71.4; mol wt, 19,500.

The ultraviolet and the infrared spectra were identical with those of the preceding preparation.

Effect of Ultraviolet Light upon PP-diprobene. A solution of 0.148 g of PP-diprobene (from perchloro-*p*-dipropenylbenzene, mp 281°) in 30 ml of purified carbon tetrachloride was placed, under nitrogen, in a quartz vessel and illuminated for 27 hr with a 500-w mercury lamp at a distance of 4 cm. The resulting solution was filtered through activated alumina, and, after elimination of the solvent by evaporation and washing with ethyl ether, an almost white powder weighing 0.122 g was obtained.

Anal. Calcd for $C_{12}Cl_{10}$: C, 28.9; H, 0.0; Cl, 71.1. Found: C, 29.1; H, 0.3; Cl, 71.3; mol wt, 13,500.

The ultraviolet and infrared spectra were identical with those of the starting material.

The same results were obtained with PP-diprobene (obtained from perchloro-*p*-dipropenylbenzene, mp 184°), mol wt, 16,500.

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[27] A significant amount of carbon tetrachloride remains strongly bound to the product and cannot be eliminated by extended heating at 100° under 0.05 mm pressure. In one case, after 2 hr at 180° under 0.2 mm pressure, carbon tetrachloride to the extent of 5% remained (weight loss and infrared spectrum). However, it can easily be eliminated by digestion of the material in boiling ethyl ether. Solvation interferes seriously with the elemental analyses.