and 3.65 (5 s, 15 H, Me-2, -12, and -18 and methyl ester-13 and -17), 4.17 and 4.29 (2 t, $J = 6$ Hz, 4 H, β-propionyl-CH_2-13 and -17), 4.80 (s, H-7^1), 6.17 (dd, $J = 2$, $J = 12$ Hz, 1 vinyl H-3), 6.33 (dd, $J = 2$, $J = 18$ Hz, 1 vinyl H-3), 7.48 and 7.90 (2 d, $J = 6$, H-7^3), H-7^4), 7.55–7.63 (m, 3 Ar H), 8.07 (dd, $J = 12$, $J = 18$ Hz, 1 vinyl H-3), 8.10–8.16 (m, 2 Ar H), 9.01, 9.34, 9.70, and 9.75 (4 s, 4 meso H); MS, *m/e* 814 (M^+), 755, 740, 672, 666, 599, and 526. Anal. Calcd for $C_{46}H_{46}N_4O_8S{\cdot}H_2O$: C, 66.34; H, 5.76; N, 6.73. Found: C, 66.57; H, 5.85; N, 6.56.

Compound 32: Vis (CH_2Cl_2) λ (nm) (ϵ) 687 (27 200), 627 (6800), 583 (11 600), 557 s (8300), 468 s (33 000), 436 br (52 700), 396 s (42 800), 350 (39 400); ^{1}H NMR δ −2.5 (s br, 2 NH), 1.75 (s, 3 H, Me-2), 2.58 (s, 3 H, methyl ester-2^1), 3.14 and 3.20 (2 t, $J = 8$ Hz, 4 H, α-propionyl-CH_2-13 and -17), 3.37, 3.47, 3.50, 3.65, and 3.66 (5 s, 15 H, Me-7, -12, and -18 and methyl ester-13 and -17), 4.15 and 4.31 (2 t, $J = 8$ Hz, 4 H, β-propionyl-CH_2-13 and -17), 4.82 (s, H-2^1), 6.14 (dd, $J = 2$, $J = 12$ Hz, 1 vinyl H-8), 6.31 (dd, $J = 2$, $J = 18$ Hz, 1 vinyl H-8), 7.48 and 7.92 (2 d, $J = 6$ Hz, H-2^3, H-2^4), 7.56–7.64 (m, 3 Ar H), 8.09 (dd, $J = 12$, $J = 18$ Hz, 1 vinyl H-8), 8.10–8.17 (m, 2 Ar H), 8.87, 9.38, 9.70 and 9.81 (4 s, 4 meso H); MS, *m/e* 814 (M^+), 755, 740, 674, 672, 500, and 599.

Acknowledgment. This work was supported by the United States National Institutes of Health (GM 29198) and the Canadian Natural Sciences and Engineering Research Council. We thank Carl Edman who carried out some of the initial studies on the acetylene reactions.

Registry No. **1**, 5522-66-7; **5**, 762-42-5; **6**, 762-21-0; **7**, 100205-63-8; **8**, 100205-64-9; **9**, 100205-66-1; **10**, 100205-67-2; **11**, 100295-94-1; **12**, 100295-95-2; **13**, 94238-43-4; **14**, 94238-24-1; **15**, 94238-35-4; **16**, 94238-25-2; **17**, 94293-60-4; **18**, 94293-59-1; **19**, 80404-53-1; **20**, 100228-57-7; **21**, 100205-65-0; **22**, 94238-23-0; **23**, 94269-75-7; **24**, 94238-27-4; **25**, 100205-68-3; **26**, 100205-69-4; **27**, 94346-19-7; **28**, 94238-29-6; **29**, 100295-96-3; **30**, 100295-97-4; **31**, 94269-76-8; **32**, 94293-61-5.

A New Synthesis, Chemical Behavior, and Spectra of Perchlorodiphenylacetylene

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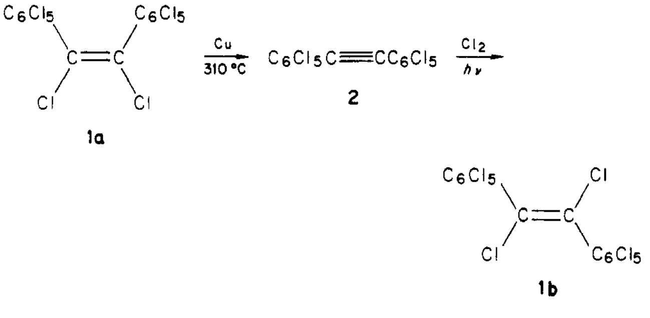
A new, high-yield synthesis of perchlorodiphenylacetylene (**2**) by dechlorination of *cis*-perchlorostilbene (**1a**) with Cu at 310 °C is described. The photochemical reaction of tolane **2** with Cl_2 or tetrachloroethylene affords *trans*-perchlorostilbene (**1b**) or mixtures of perchloro-1,2-diphenylcyclobutene (**3**) and perchloro-1,2-dihydrocyclobuta[*l*]phenanthrene (**4**), respectively. The thermal dimerization of tolane **2** at 350 °C gives a mixture of perchloro-1,2,3-triphenylnaphthalene (**5**), perchloro-2,3,8-triphenylbenzofulvene (**6**), and perchloro-5,10-diphenylideno[2,1-*a*]indene (perchloro-5,10-diphenyldibenzo[*a*,*e*]pentalene (**7**)). Fulvene **6** dechlorinates to indenoindene **7** under stronger reaction conditions. Naphthalene **5** photochlorinates with Cl_2 to perchloro-1,2,3-triphenyl-3,4-dihydronaphthalene (**8**), which reverts to naphthalene **5** at 190 °C. The reaction of tolane **2** with oleum gives perchloro-α,α'-dihydroxystilbene cyclic sulfate (**12**), which decomposes thermally (220 °C) yielding perchlorodiphenylethanedione (**14**). The hydrolysis of dihydronaphthalene **8** affords perchloro-4,5,6-triphenylindenone (**18**). The mechanisms of some unusual reactions, as well as the IR and UV–vis spectra of the new compounds, are presented and discussed.

It has been emphasized earlier[1] that the perchlorophenylethylenes, such as perchlorostyrene,[2,3] the perchlorostilbenes,[4] and the perchloropolyarylethylenes,[5] are passive toward addition reactions. In contrast, perchlorophenylacetylene displays a remarkable reactivity.[1] The main reason for such a difference of behavior is of steric nature: While the adducts of perchlorophenylethylenes are, or should be, sterically strained, distorted molecules,[6,7] the ethylenes resulting from perchlorophenylacetylenes would be essentially strain-free molecules.

If perchlorophenylacetylene displays any steric effect at all, it is some shielding of the acetylene carbon bonded to the benzene ring. In fact, some of its reactions have been explained in terms of such a shielding, which, however, appears ineffectual in intramolecular processes.[1]

Scheme I



Therefore, it was regarded as significant to undertake a study on the synthesis and behavior of perchlorotolane (perchlorodiphenylacetylene) where *both* acetylene carbons are shielded by the neighbouring (ortho) chlorines.[8]

Results and Discussion

Perchlorotolane (2) (Scheme I). Perchlorotolane (**2**) has been synthesized in an excellent yield by dechlorination of *cis*-perchlorostilbene (**1a**)[4] with copper, at 310 °C. Tolane **2** had been obtained before[4,10] in ways other than

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0022-3263/86/1951-1100$01.50/0

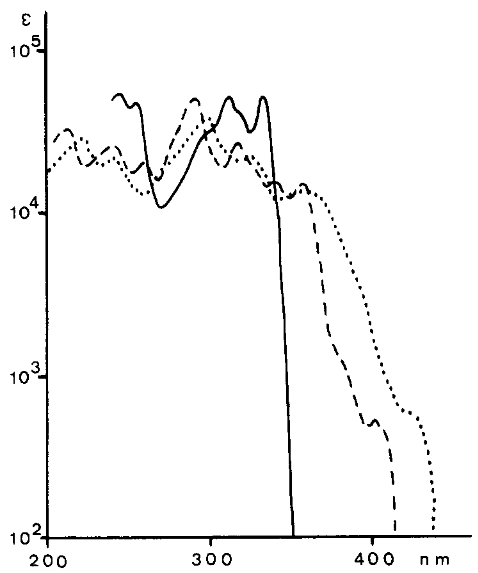
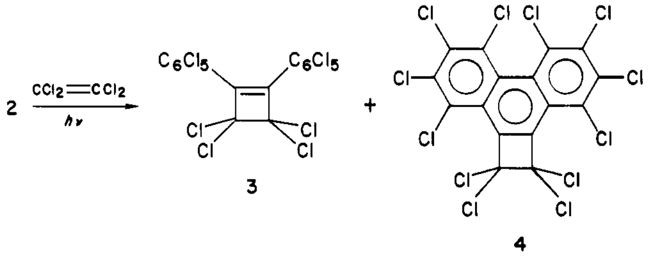


Figure 1. UV spectrum of perchlorotolane (1) (—), perchloro-1,2-dihydrocyclobutaphenanthrene (4) (- - -), and perchlorophenanthrene (···).

Scheme II



that here described. However, not only was its characterization incomplete but also the reported UV absorptivities were erroneous by a factor of 40.[10] Its spectrum (Figure 1) shows a dentate fine structure in the intense conjugation band (~320 nm) which is characteristic of the highly chlorinated phenylacetylenes.[1,11] It is noteworthy that while in perchlorophenylacetylene that intense band is centered around 270 nm,[1] and the relatively weak secondary (^1L_b) band appears about 310 nm,[12] in tolane 2, on account of the extended π-electron delocalization, the conjugation band is found around 320 nm, swamping completely the secondary band.

Chlorine Addition to Tolane 2 (Scheme I). Chlorine adds to tolane 2 under the influence of incandescent white light, in CCl_4, giving an almost quantitative yield of *trans*-perchlorostilbene (**1b**), which had been synthesized before by reductive condensation of perchlorotoluene.[4]

Perchloroethylene Addition to Tolane 2 (Scheme II). A solution of tolane 2 in perchloroethylene gives, under illumination with UV light, a mixture of perchloro-1,2-diphenylcyclobutene (**3**) and perchloro-1,2-dihydrocyclobuta[*l*]phenanthrene (**4**). Under similar conditions, a cyclization yielding the biphenyl system, as in phenanthrene 4, takes place in perchlorotriphenylmethyl radical where two of its pentachlorophenyl rings condense, with elimination of chlorine, giving perchloro-9-phenylfluorenyl radical.[13,14] This suggests that the cyclization to phenanthrene 4 might occur through an excited state radical mechanism.

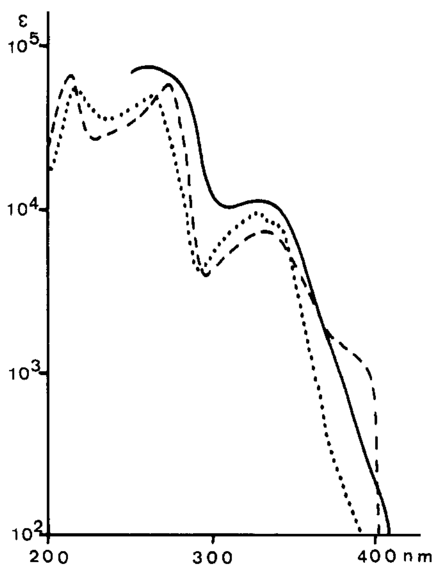


Figure 2. UV spectrum of perchloro-1,2,3-triphenylnaphthalene (**5**) (—), perchloro-1-phenylnaphthalene (···), and perchloro-2-phenylnaphthalene (- - -).

The structure of chlorocarbons 3 and 4 has been fully established by elemental analyses, and IR, UV–vis, and mass spectral data. In this connection it is pointed out that photoaddition of perchloroethylene to perchlorophenylacetylene giving a perchlorodiphenylcyclobutene has recently been described.[1] The IR spectrum of cyclobutene 3 is that of an alkylaromatic chlorocarbon, with a weak first benzenoid peak (1525 cm^{-1}) and a group of intense second benzenoid peaks centered about 1350 cm^{-1}.[15] As expected, no C=C stretching is observed (tetrasubstitution).

As in other fused polycyclic aromatic chlorocarbons, the IR of phenanthrene 4 displays a peak in the region where benzene chlorocarbons do not absorb (1500–1400 cm^{-1}).[15] Its UV–vis spectrum is similar to that of perchlorophenanthrene[16] (Figure 1), being somewhat (10–20 nm) displaced hypsochromically. This shift is most probably due to the "in-plane" molecular strain in the aromatic system caused by the presence of a cyclobutene ring. In fact, the secondary (^1L_b) band of "in-plane"-strained benzene derivatives, such as benzocyclobutene[17] and perchlorobenzocyclobutene,[18] show definite hypsochromic shifts with respect to comparable, nonstrained counterparts.

Thermal Dimerization of Tolane 2 (Scheme III). By heating tolane 2 at about 250 °C, an excellent conversion to three dimeric chlorocarbons is obtained. The main product is perchloro-1,2,3-triphenylnaphthalene (**5**). A substantial yield of (*Z*)-perchloro-2,3,8-triphenylbenzofulvene (**6**) and a small proportion of perchloro-5,10-diphenyldibenzo[*a*,*e*]pentalene (perchloro-5,10-diphenylindeno[2,1-*a*]indene (**7**) are also obtained. Under the dimerization conditions, fulvene 6 cyclizes slowly to pen-

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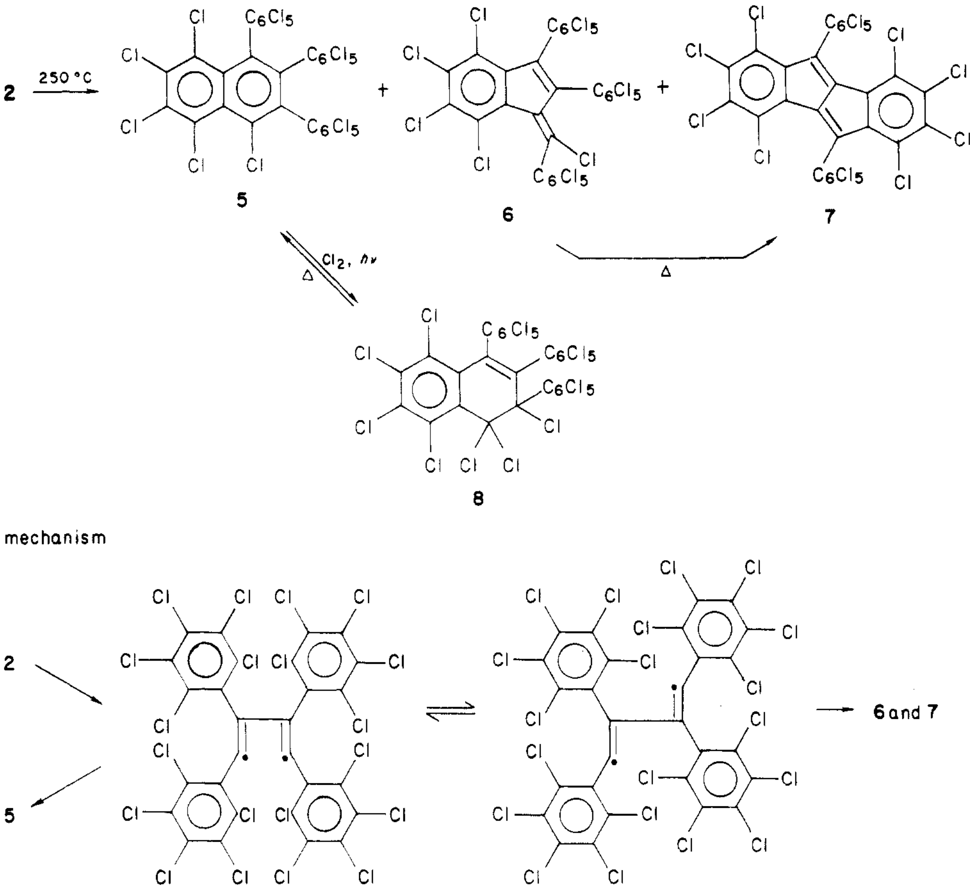
Scheme III



talene 7, this cyclization being accelerated by powdered aluminum and higher temperatures, affording excellent yields.

Naphthalene 5 has been characterized by elemental analyses, IR and UV spectroscopy, and mass spectrometry. Its structure has been established unambiguously by X-ray diffraction analysis.[19] Its IR spectrum displays the characteristic peak at 1405 cm^{-1} found in fused polycyclic aromatic chlorocarbons, as in phenanthrene 4, and the peak group around 1350 cm^{-1} due to the pentachlorophenyl substituents.[15] The UV spectrum of naphthalene 5 shows an intense band at about 330 nm, as in perchloronaphthalene, perchloro-1-phenylnaphthalene and perchloro-2-phenylnaphthalene[16] (Figure 2).

Pentalene 7 has been characterized by IR and UV–vis spectroscopy and mass spectrometry. As expected, the UV–vis spectrum is very similar to that of Roedig's perchlorodibenzo[*a*,*e*]pentalene.[20] Its structure has been ascertained unambiguously by X-ray diffraction.[21]

The structure and configuration of fulvene 6 has been established on the basis of its thermal cyclization to pentalene 7 and IR[15] and mass spectra.

A reasonable biradicaloid mechanism for such dimerizations is shown in Scheme III, as postulated in the dimerization of perchlorophenylacetylene.[1] In contrast with the oligomerization of perchlorophenylacetylene,[1] no trimers are found here, since it was expected on steric grounds that the addition of a third molecule to a dimer should be severely hindered. Notice that such cyclizations involve a chlorine atom shift.

Chlorination of naphthalene 5 with chlorine and white, incandescent light, in cold CCl_4, gives perchloro-3,4-dihydro-1,2,3-triphenylnaphthalene (8) in a good yield (Scheme III). This is a rather thermally sensitive chlorocarbon which reverts slowly to 5 in boiling CCl_4 and results in an excellent yield at 190 °C.

The structure of chlorocarbon 8 has been assigned mainly on the basis of the *absence* of an IR peak in the neighborhood of 1600 cm^{-1}, which indicates that two pentachlorophenyl groups are attached to its ethylene group. (In contrast, dihydrochlorocarbons, such as perchloro-1,4-dihydro-6-phenylnaphthalene,[16] perchlorostyrene,[3,15] and perchloroindene,[15,22] *do show* a C=C stretching peak at 1645, 1610, and 1587 cm^{-1}, respectively.) The possibility of this dihydronaphthalene being the 1,4-dihydro isomer is ruled out since its UV spectrum displays an intense (ϵ 10 500) conjugation (styrene) band, as in perchloroindene (ϵ 39 000),[22] while perchloro-6-phenyl-1,4-dihydronaphthalene[16] does not show such a band but an absorption minimum in such a vicinity. In this connection it is pointed out that no significant conjugation of the pentachlorophenyl rings with the ethylene bond is possible in 8 since on account of strong steric repulsions among the neighboring substituents, those rings are nearly perpendicular to the plane of the ethylene system. This type of steric inhibition of resonance is also found, in a variable degree, in perchloro-1,1-diphenylethylene,[23] the perchlorostilbenes,[4] and even in perchlorostyrene.[24] In fact, the X-ray data of naphthalene 5 show that the pentachlorophenyl groups are nearly orthogonal to the mean

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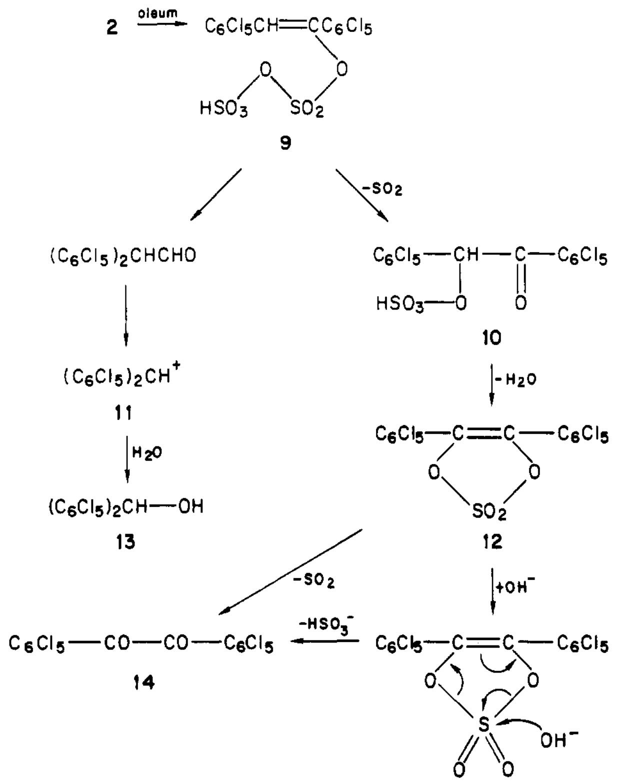
Scheme IV



plane of the naphthalene system.[19]

The low thermal stability of dihydronaphthalene **8** is circumstantial evidence for its own sterically strained molecular structure. In fact, the repulsions among the bulky substituents bonded to the 3-(sp^3)carbon (a chlorine, a pentachlorophenyl, and two carbons attached to a second pentachlorophenyl and two chlorines) are severe, comparable to those in perchlorotoluene, a paradigm of sterically strained, distorted, and consequently labile chlorocarbon.[6,7]

Reaction of Tolane 2 with Oleum (Scheme IV). While perchlorophenylacetylene reacts with concentrated H_2SO_4, giving water-addition products,[1] tolane **2** does not. This might be due to the extremely low solubility of the latter. However, with 65% oleum at 100 °C, an oxidative addition takes place affording 4,5-bis(pentachlorophenyl)-1,3,2-dioxathiole 2,2-dioxide (**12**) (cyclic α,α'-dihydroxystilbene sulfate). This sulfate has been characterized by elemental analyses and spectra. Its UV spectrum is, as expected, similar to that of *cis*-perchlorostilbene,[4] displaying the conjugation and the secondary bands nearly at the same wavelengths.

When the reaction is carried out with a weaker oleum (20%), some tolane **2** is recovered, sulfate **12** is obtained, and a small proportion of bis(pentachlorophenyl)carbinol[25] (**13**) is isolated. A blue color develops immediately, the relevant visible spectrum being coincident (maximum, 600 nm; minimum, 475 nm) with that resulting of dissolving carbinol **13** in oleum. This colored species is presumably the αH-decachlorodiphenylcarbenium ion (**11**).

A reasonable explanation of such remarkable oxidation reactions is also given in Scheme IV: The first step would be the formation of enol disulfate **9**, which would eliminate SO_2, giving benzoin sulfate **10**, and next cyclize with water elimination to give cyclic sulfate **12**. Some disulfate **9** (or sulfate) would undergo a pinacol rearrangement, via migration of a pentachlorophenyl group, to a bis(pentachlorophenyl) derivative, which would next undergo a degradative oxidation to carbenium ion **11**, and finally to carbinol **13**.

Cyclic sulfate **12** is converted easily to perchlorobenzil[26] (**14**) in an excellent yield, by heating above 220 °C. This type of SO_2 elimination has been observed in diphenol cyclic sulfates, giving *o*-quinones.[27] Such a conversion can also be effected by treatment with NaOH in an aqueous solvent. We favor the given mechanism, consisting in an one-step nucleophilic displacement on sulfur. In this connection, some related results have been taken into account.[28-30]

Reaction of Dihydronaphthalene 8 with Oleum (Scheme V). A fair conversion of dihydronaphthalene **8** to perchloro-4,5,6-triphenylindenone (**18**) is obtained by treatment with oleum (100 °C). The latter has been characterized as usual. Its UV-vis spectrum presents the bands located nearly at the same wavelengths as perchloroindenone.[31]

Under the same conditions, a similar oxidative degradation takes place starting from perchloro-9,10-dihydrophenanthrene, which undergoes successively solvolysis to perchlorophenanthrene-9,10-quinone, oxidative ring-opening to perchlorobiphenyl-2,2′-dicarboxylic acid, and decarboxylative ring closure to perchlorofluorenone.[16] Analogously, the following crucial considerations and mechanistic steps for the formation of indenone **18** are suggested, which in turn provide structural evidence for the latter and intermediates:

(a) The first step of the reaction of dihydronaphthalene **8** with oleum is the formation of a carbenium ion, where the 3-chlorine is preferentially eliminated. It is pointed out that elimination of the 4-chlorine would create additional molecular strain due to strong steric repulsions between the remaining 4-chlorine and the 5-chlorine. (To minimize the molecular strain of **8**, the 5-chlorine must be geared in with the two 4-chlorines.)

(b) The formal positive charge in the 3-carbon of carbenium ion **15** is delocalized mainly on the carbons 1, 6, and 8. Nucleophilic attack of disulfuric acid at the 1- and 8-carbons is sterically hindered, while that at the 6-carbon *is not*.

(c) The warping of the rings in ketone **16**, due to the loss of the aromatic character of the bicyclic grouping now allows the removal of one 4-chlorine to form ketone–carbenium ion **17** with no significant additional steric repulsions between the 5-chlorine and the remaining 4-chlorines. The positive charge of such a ketone–carbenium ion would be delocalized mainly on the potentially active positions 4, 5, and 7. The aromaticity of intermediates and products deriving from a nucleophilic attack on the 5-carbon is regarded as a decisive factor. In fact, such an attack is the only one that can lead to the indenone.

The product is therefore the perchloro-4,5,6-triphenylindenone (**18**), not its 5,6,7-triphenyl isomer.

Experimental Section

General Methods. The IR, UV-vis, and mass spectra have been recorded with Perkin-Elmer 457, Beckman Acta M VI, and AEI MS-902S spectrometers, respectively.

Perchlorotolane (2). A mixture of *cis*-perchlorostilbene[4] (**1a**) (0.201 g) and powdered Cu (0.808 g) was heated (130 °C; 1 h) under vacuum, argon was introduced, and it was heated further (310

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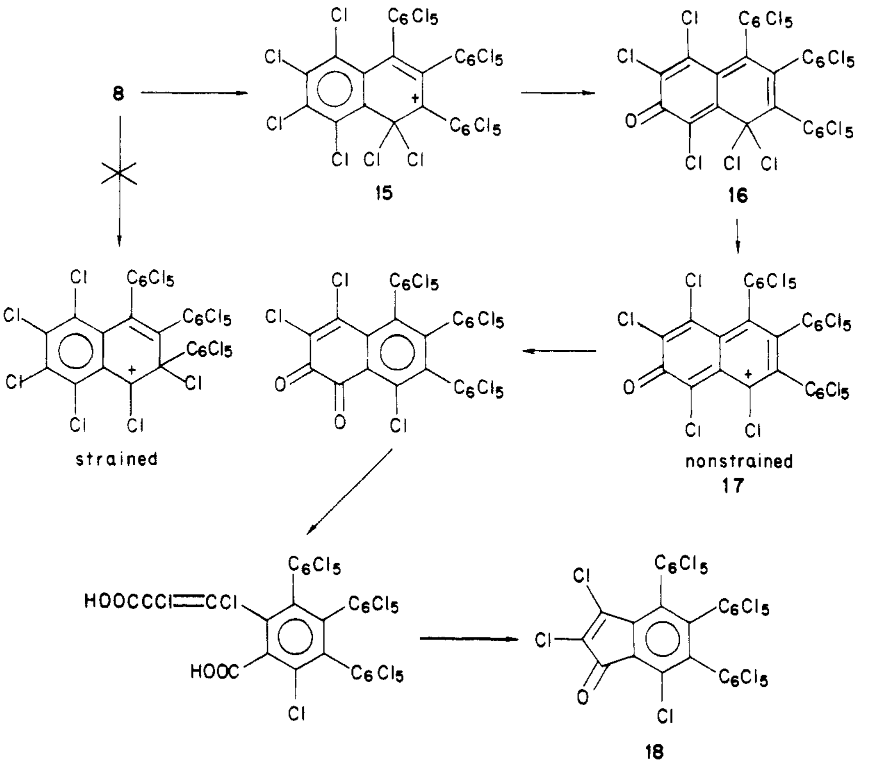
Scheme V



°C; 50 min). The resulting mass was continuously extracted with refluxing $CHCl_3$ (4 days). The resulting white, almost insoluble, powder was identified as tolane **2** (0.160 g; 90%): mp 356-357 °C (lit.[10] mp 359 °C); IR (KBr) 1428 (m), 1350 (s), 1315 (m), 1270 (s), 772 (s), 718 (s) cm^{-1}; UV ($CHCl_3$) (Figure 1) 245 nm, 254, 295 (sh), 303 (sh), 314, 320 (sh), 335 (ϵ 39 800, 35 800, 21 500, 25 800, 40 300, 31 100, 39 600); MS (all ^{35}Cl), *m/z* 518 ($C_{14}Cl_{10}^+$), 448 ($C_{14}Cl_8^+$), 378 ($C_{14}Cl_6^+$). Anal. Calcd for $C_{14}Cl_{10}$: C, 32.1; Cl, 67.8. Found: C, 32.1; Cl, 67.7.

Chlorination of Tolane 2. A stream of dry Cl_2 was passed (22 h) through a suspension of tolane **2** (0.100 g) in refluxing CCl_4 (90 ml) while being illuminated with a 500-W incandescent lamp at 20 cm from the Pyrex flask. Elimination of the solvent and digestion of the residue with boiling hexane gave *trans*-perchlorostilbene[4] (**1b**) (0.109 g; 96%), identified by its mp and IR spectrum.

Reaction of Tolane 2 with Tetrachloroethylene. A solution of tolane **2** (0.095 g) in tetrachloroethylene 450 mL) was irradiated (24 h) with 16 Rayonet UV lamps (20 W each; 3000 Å) at room temperature and under nitrogen. Evaporation of the solvent gave an orange residue, which by crystallization from $CHCl_3$ yielded starting material **2** (0.056 g; 59% recovery). The mother liquors were evaporated and the residue, passed through silica gel in CCl_4 and submitted to fractional crystallization, afforded the following. (a) Perchloro-1,2-dihydrocyclobuta[*l*]phenanthrene (**4**) (0.020 g; 18%): orange crystals, mp 297 °C dec; IR (KBr) 1500 (w), 1440 (w), 1368 (w), 1355 (m), 1344 (w), 1334 (m), 1302 (s), 1265 (m), 1088 (s), 995 (s), 916 (s), 825 (s), 775 (m), 754 (s), 715 (m), 615 (m), 596 (m), 576 (m), 560 (m), 510 (s), 490 (s) cm^{-1}; UV-vis (C_6H_{12}) (Figure 1) 212 nm, 242, 261, 290, 318, 329 (sh), 342, 357, 382 (sh), 404 (ϵ 30 100, 25 400, 20 300, 48 200, 26 800, 18 400, 15 600, 15 000, 1240, 521); MS (all ^{35}Cl), *m/z* 612 ($C_{16}Cl_{12}^+$), 577 ($C_{16}Cl_{11}^+$), 542 ($C_{16}Cl_{10}^+$), 472 ($C_{16}Cl_8^+$), 402 ($C_{16}Cl_6^+$). (b) Perchloro-1,2-diphenylcyclobutene (**3**) (0.009 g; 7%): white crystals, mp 211 °C dec; IR (KBr) 1525 (w), 1355 (w), 1338 (s), 1321 (m), 1272 (m), 1084 (m), 847 (m), 765 (s), 518 (m) cm^{-1}; MS (all ^{35}Cl), *m/z* 682 ($C_{16}Cl_{14}^+$), 612 ($C_{16}Cl_{12}^+$), 542 ($C_{16}Cl_{10}^+$), 518 ($C_{14}Cl_{10}^+$).

Thermal Dimerization of Tolane 2. (1) Tolane **2** (4.00 g) was heated (350-360 °C; 45 min) under N_2 in a sealed glass tube. The resulting reddish brown mass was digested in CCl_4 and submitted to a cumbersome fractional crystallization ($CHCl_3$, CCl_4, and hexane) and chromatography on silica gel (same solvents) to give the following. (a) Starting material **2**: 1.054 g; 26% recovery. (b) Perchloro-1,2,3-triphenylnaphthalene (**5**) (1.668 g; 42%): white crystals, mp 346 °C; IR (KBr) 1530 (w), 1405 (w), 1385 (w), 1370 (w), 1340 (s), 1320 (s), 1300 (s), 1270 (s), 825 (m), 790 (m), 775 (s), 765 (s), 735 (m), 710 (s), 690 (m), 555 (m), 519 (m), 480 (m) cm^{-1}; UV (C_6H_{12}) (Figure 2) 271 nm, 322 (sh), 335 (ϵ 54 200, 9960, 10 600); MS (all ^{35}Cl), *m/z* 1036 ($C_{28}Cl_{20}^+$), 966 ($C_{28}Cl_{18}^+$), 896 ($C_{28}Cl_{16}^+$), 826 ($C_{28}Cl_{14}^+$), 413 ($C_{28}Cl_{14}^{2+}$), 378 ($C_{28}Cl_{12}^{2+}$), 343 ($C_{28}Cl_{10}^{2+}$). Anal. Calcd for $C_{28}Cl_{20}$: C, 32.1; Cl, 67.9. Found: C, 32.1; Cl, 67.6. (c) Perchloro-2,3,8-triphenylbenzofulvene (**6**) (1.244 g; 31%): yellow powder, dec 367 °C (DSC exothermic peak); IR (KBr) 1590 (w), 1520 (w), 1370 (s), 1345 (s), 1318 (s), 1290 (m), 1240 (m), 848 (m), 820 (m), 796 (m), 789 (m), 775 (m), 768 (m), 760 (m), 720 (m), 710 (m), 685 (m), 668 (m) cm^{-1}; UV-vis (C_6H_{12}) 275 nm, 360 (ϵ 39 300, 7500); MS (all ^{35}Cl), *m/z* 1036 ($C_{28}Cl_{20}^+$), 966 ($C_{28}Cl_{18}^+$), 413 ($C_{28}Cl_{14}^{2+}$), 378 ($C_{28}Cl_{12}^{2+}$), 343 ($C_{28}Cl_{10}^{2+}$). Anal. Calcd for $C_{28}Cl_{20}$: C, 32.1; Cl, 67.9. Found: C, 32.0; Cl, 67.9. (d) Perchloro-5,10-diphenylindeno[2,1-*a*]indene (perchloro-5,10-diphenyldibenzo[*a*,*e*]pentalene) (**7**) (0.040 g; 1%); red crystals, mp >350 °C; IR (KBr) 1615 (w), 1535 (w), 1385 (s), 1348 (s), 1320 (m), 1300 (m), 1262 (s), 1160 (m), 807 (s), 790 (m), 770 (m), 713 (m), 670 (m), 630 (m) cm^{-1}; UV-vis (C_6H_{12}) 217 nm, 244 (sh), 300, 312, 397 (sh), 423, 448, 480 (ϵ 142 800, 54 100, 59 300, 77 500, 3060, 7900, 16 200, 16 800); MS (all ^{35}Cl), *m/z* 966 ($C_{28}Cl_{18}^+$), 896 ($C_{28}Cl_{16}^+$), 826 ($C_{28}Cl_{14}^+$), 483 ($C_{28}Cl_{18}^{2+}$), 413 ($C_{28}Cl_{14}^{2+}$). Anal.[32] Calcd for $C_{28}Cl_{18}$: C, 34.4; Cl, 65.6. Found: C, 34.2; Cl, 65.3. The overall yield is therefore quantitative.

(2) The preceeding reaction was repeated with a 2-h reaction time. The resulting products were as follows: (a) tolane **2** (9% recovery); (b) naphthalene **5** (30%); (c) fulvene **6** (10%); (d) pentalene **7** (23%). The overall yield is lower due to a greater difficulty in the separation of the products in state of purity.

Dechlorination of Fulvene 6. (**a**) Compound **6** (0.050 g) was heated (370 °C; 10 min) under argon in a sealed glass tube. The resulting mass was passed through silica gel in CCl_4 and crystallized from $CHCl_3$-hexane to give starting material **6** (0.030 g; 60% recovery) and pentalene **7** (0.008 g; 16%).

(**b**) A mixture of fulvene **6** (0.050 g) and powdered Al (0.025 g) was heated and treated as in the preceding paragraph to give pentalene **7** (0.042 g; 81%).

Chlorination of Naphthalene 5. The chlorination of naphthalene **5** (0.190 g) was carried out as in the case of tolane **2**.

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[32] This compound crystallized with 1 mol of CCl_4 as ascertained by IR and X-ray[21] analyses. In order to obtain an analytical sample, it must be dried at high vacuum [260 °C (0.4 mmHg); 4 h].

Evaporation of the solvent gave a residue, which by crystallization from benzene yielded perchloro-1,2,3-triphenyl-3,4-dihydronaphthalene (**8**) (0.112 g): mp 185 °C dec; IR (KBr) 1530 (w), 1400 (w), 1380 (w), 1338 (s), 1318 (s), 860 (m), 830 (m), 810 (m), 755 (s), 730 (m), 710 (s) cm^{-1}; UV (C_6H_{12}) 218 nm, 229, 280 (sh), 307 (sh) (ϵ 73 500, 73 400, 10 500, 3930). Anal.[33] Calcd for $C_{28}Cl_{22}\cdot{}^1/_2C_6H_6$: C, 32.2; H, 0.3; Cl, 67.5. Found: C, 32.2; H, 0.5; Cl, 67.2. Evaporation of the mother liquors gave a residue, which by TLC (silica gel, CCl_4) afforded more dihydronaphthalene **8** (0.035 g; 72% overall yield) and starting naphthalene **5** (0.020 g; 10% recovery).

Thermal Dechlorination of Dihydronaphthalene 8. Compound **8** (0.030 g) was heated (190 °C; 10 min) under argon in a sealed glass tube. The resulting mass was passed through silica gel in CCl_4 to give naphthalene **5** (0.026 g; 93%). This dechlorination can be effected slowly (days) in boiling CCl_4.

Reaction of Tolane 2 with Oleum. (1) A mixture of tolane **2** (0.500 g) and 20% oleum (300 mL) was heated (100 °C; 24 h) with stirring. The resulting mixture was poured into ice and extracted with $CHCl_3$. The organic extract was dried and concentrated to a small volume, giving a white precipitate that was identified as starting material (0.212 g; 42%). Evaporation of the solvent gave a yellowish residue (0.196 g), which by TLC (silica gel; $CHCl_3$) afforded the following. (a) Starting material: 0.021 g; 4%. (b) 4,5-Bis(pentachlorophenyl)-1,3,2-dioxathiole 2,2-dioxide (α,α'-dihydroxydecachlorostilbene cyclic sulfate) (**12**) (0.123 g; 21%): white crystals, mp 230 °C dec; IR (KBr) 1530 (w), 1430 (s), 1350 (m), 1315 (m), 1275 (m), 1220 (s), 1157 (m), 1078 (m), 1010 (m), 795 (s), 725 (m), 718 (m), 698 (m) cm^{-1}; UV (C_6H_{12}) 224 nm, 243 (sh), 284, 304 (sh) (ϵ 49 000, 28 800, 10 100, 4390); MS (all ^{35}Cl), m/z 275 ($C_7Cl_5O^+$), 247 ($C_6Cl_5^+$), 212 ($C_6Cl_4^+$), 177 ($C_6Cl_3^+$). Anal. Calcd for $C_{14}Cl_{10}O_4S$: C, 27.2; Cl, 57.3;, S, 5.2. Found: C, 27.1; Cl, 57.5; S, 4.9. In one experiment, a small proportion of bis(pentachlorophenyl)carbinol (**13**) was isolated, which was identified by its mp [285–90 °C dec (lit.[25] mp 281–89 °C dec)] and IR spectrum.[25]

(2) This reaction was repeated with 65% oleum (50 ml) and tolane **2** (0.100 g) at room temperature (48 h). Cyclic sulfate **12** (0.090 g; 76%) was obtained.

Thermolysis of Cyclic Sulfate 12. Compound **12** was heated (250 °C; 2 h) in a sealed glass tube. The yellow residue was purified through silica gel in CCl_4, yielding perchlorodiphenylethanedione (perchlorobenzil) (**14**) (0.040 g; 89%): yellow crystals, mp 312–315 °C (lit.[26] mp 310.5–311.0 °C); IR (KBr) 1725 (s), 1530 (w), 1348 (s), 1334 (s), 1309 (w), 1230 (s), 1130 (s), 951 (s), 800 (m), 700 (s), 656 (m) cm^{-1}; UV (C_6H_{12}) 212 nm, 238, 290, 298, 315 (sh) (ϵ 99 200, 25 900, 2020, 1990, 1420); MS (all ^{35}Cl), m/z 275 ($C_7Cl_5O^+$), 247 ($C_6Cl_5^+$), 212 ($C_6Cl_4^+$), 177 ($C_6Cl_3^+$). Anal. Calcd for $C_{14}Cl_{10}O_2$: C, 30.3; Cl, 63.9. Found: C, 30.3; Cl, 63.8.

Hydrolysis of Cyclic Sulfate 12. (1) A mixture of cyclic sulfate **12** (0.050 g), acetonitrile (10 mL), and aqueous 0.01 N NaOH (7 mL) was refluxed (3 h) with stirring. The resulting mixture was extracted with $CHCl_3$, and the organic layer was washed with water, dried with Na_2SO_4, and evaporated. The resulting solid by fractional crystallization from hexane gave starting material (0.025 g; 50% recovery) and benzil **14**[26] (0.018 g; 40%).

(2) A mixture of cyclic sulfate **12** (0.050 g), dioxane (40 mL), and aqueous 0.01 N NaOH (9 mL) was stirred (6 h) at room temperature. The resulting mixture was diluted with water and treated as in the preceeding paragraph to give starting material **12** (0.017 g; 34% recovery) and benzil **14** (0.018 g; 40%).

Reaction of Dihydronaphthalene 8 with Oleum. A mixture of dihydronaphthalene **8** (0.200 g) and 20% oleum (70 ml) was heated (100 °C; 24 h) with stirring. The resulting mass was poured into ice and extracted with $CHCl_3$. The organic extract was washed with water, dried with Na_2SO_4, and evaporated. The residue by TLC (SiO_2, CCl_4) gave starting material **8** (0.053 g; 26.5% recovery) and perchloro-4,5,6-triphenylinden-1-one (**18**) (0.052 g; 30%): yellow crystals, mp 286 °C dec; IR (KBr) 1732 (s), 1580 (w), 1550 (w), 1532 (w), 1334 (s), 1316 (s), 1188 (m), 981 (m), 860 (m), 831 (m), 800 (m), 787 (s), 710 (m), 692 (m), 678 (m) cm^{-1}; UV–vis ($CHCl_3$) 238 nm, 246 (sh), 268 (sh), 355, 370, 408 (sh) (ϵ 63 000, 58 400, 38 500, 2220, 2120, 1120); MS (all ^{35}Cl), m/z 970 ($C_{27}Cl_{18}O^+$), 935 ($C_{27}Cl_{17}O^+$), 397.5 ($C_{27}Cl_{13}O^{2+}$), 366 ($C_{26}Cl_{12}^{2+}$), 331 ($C_{26}Cl_{10}^{2+}$). Anal. Calcd for $C_{27}Cl_{18}O$: C, 33.1. Found: C, 33.1.

Registry No. **1a**, 76570-98-4; **1b**, 52789-10-3; **2**, 20094-80-8; **3**, 100231-15-0; **4**, 100231-16-1; **5**, 66341-44-4; **6**, 100231-17-2; **7**, 72760-93-1; **8**, 100231-18-3; **12**, 100231-19-4; **13**, 33240-66-3; **14**, 19349-29-2; **18**, 100231-20-7; tetrachloroethylene, 127-18-4.

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[33] This compound crystallized with $^1/_2$ mol of benzene that could not be eliminated by drying at high vacuum.

Proton Affinities of Azoles: Experimental and Theoretical Studies

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The proton affinities (PA's) of a series of azoles as measured by pulsed high-pressure mass spectrometry are (in kcal/mol) isoxazole, 202.3; oxazole, 207.8; 1,2,4-triazole, 212.4; pyrazole, 212.8; thiazole, 213.2; imidazole, 222.1; 4-methylimidazole, 224.8; 1-methylimidazole, 228.0. Ab initio protonation enthalpies calculated at the MP2/6-31G(d,p) level reproduce the above order and give approximate numerical values. Additionally, these calculations show that the protonation sites are N_3 in imidazole and oxazole and N_4 in 1,2,4-triazole, the alternate protonation sites of N_1, O, and N_2, respectively, being less favorable by 53, 57, and 13 kcal/mol. These ab initio studies also indicate a correlation between lone pair n orbital energies and proton affinities.

Azoles are a large and important class of heterocycles that are often found as components of enzymes and coenzymes as well as in numerous pharmaceuticals, dyes, and explosives. Azoles are also starting materials for the synthesis of a variety of complex natural and synthetic species. Much of the interesting chemistry and biochemistry of azoles arises from their properties as bases, since they may undergo protonation or hydrogen bonding in acidic media.

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