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Synthesis and Chemical Behavior of Perchlorophenylacetylene

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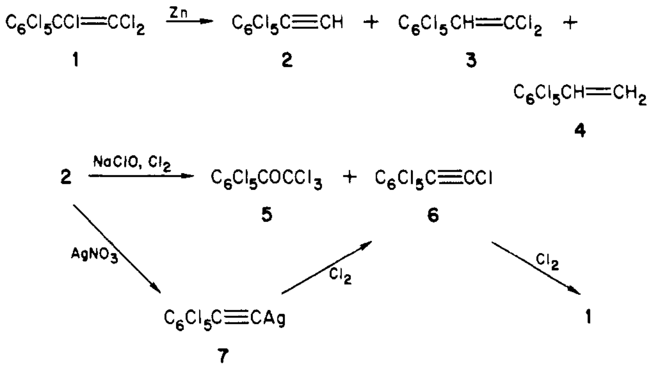
Perchlorophenylacetylene (**6**) is synthesized in three steps: (1) vicinal reductive dechlorination of perchlorostyrene (**1**) to (pentachlorophenyl)acetylene (**2**), (2) conversion of **2** into its silver acetylide (**7**), and (3) chlorination of **7** to **6**. Some thermal and photochemical reactions of **6** are reported—including chlorine, cyclohexane, hydrogen chloride, water, methanol, perchloroethylene, and trichloroethylene additions—which yield either directly or indirectly the following highly chlorinated products: αH-hexachloro-β-(cyclohexyl)styrene (**10**), isomeric *cis*- and *trans*-βH-heptachlorostyrenes (**11**), $\alpha H,\alpha H$-hexachloroacetophenone (**12**), (pentachlorophenyl)acetic acid (**13**), methyl (pentachlorophenyl)acetate (**17**), $\alpha H,\beta$-methoxyhexachlorostyrene (**16**), perchloro-1-phenylcyclobutene (**18**), perchloro-2-phenylbutadiene (**19**), perchlorophenylmaleic acid (**20**), **20** dimethyl ester (**21**), **20** anhydride (**22**), 3(or 4)H-nonachloro-1-phenylcyclobutene (**23**), 1H-nonachloro-3-phenylbutadiene (**24**), and a perchlorodiphenylbicyclo[4.2.0]octa-2,4,7-triene (**25**). The thermal (110–210 °C) oligomerization of **6** yields perchloro-1-phenylnaphthalene (**27**), perchloro-1,2,3- (**28**) and perchloro-1,2,4-triphenylbenzene (**29**), perchloro-1,4-diphenylbutenyne (**30**), and a trimer of unknown structure. The formation of trimers is interpreted by assuming the intermediacy of substituted-benzene valence isomers.

Since the first synthesis of perchlorotoluene[1,2] and the relevant discovery of reagent BMC,[2,3]—a most powerful yet selective perchlorinating agent—a considerable effort has been performed by our group for the development of perchloro organic chemistry,[4-7] which was previously regarded as a deserted, barren field. Some perchlorocompounds, such as the alkylaromatic chlorocarbons, are highly strained, distorted molecules, and therefore reactive, while other are extremely stable, both chemically and thermally. In fact, perchlorophenylethylenes, such as perchlorostyrene,[8] the perchlorostilbenes,[9] and the so-called "PP-polymers",[10] possess a very high thermal stability (up to and beyond 500 °C, in air) and are extremely inert toward addition reactions, even toward highly aggressive chemical species (fuming HNO_3, oleum, Cl_2, etc.). This has been traced to deactivation by the electronegative chlorines toward electrophilic attack, to steric shielding of the ethylene bond by the neighboring bulky chlorines, and to the forbidding molecular steric strain of the would-be adducts.[2,4,11-14]

The perchlorophenylacetylenes should behave differently, since their steric molecular features *are* intrinsically different. Space-filling scale atomic models indicate that the shielding of the ethyne group by the ortho chlorines of the aryl rings, though significant, is not forbidding, and that the would-be adducts (ethylenes), although strongly resonance-inhibited, are unstrained and undistorted. A practical aspect of this might be the use of certain perchloroarylacetylenes as stable intermediates or precursors in syntheses within perchloro organic chemistry. Therefore, it was decided to attempt the preparation of the simplest chlorocarbon of this type, perchlorophenylacetylene (**6**),[15] and to study some aspects of its chemical behavior. This synthesis has been achieved from (pentachlorophenyl)acetylene (**2**).

Scheme I



Syntheses of (Pentachlorophenyl)acetylene (2) (Scheme I). The electrolytic reduction of perchlorostyrene (**1**) had been performed by Seiber, giving, under optimal conditions, (pentachlorophenyl)acetylene (**2**) in excellent yield, αH-heptachlorostyrene (**3**) and $\omega H,pH$-tetrachlorophenylacetylene being also formed.[17] Here are reported some chemical dechlorinations of styrene **1** with Zn, or with Mg. When activated (with aqueous HCl) Zn in dioxane is used, excellent yields of acetylene **2** are obtained. However, if the reaction is not performed under rigorous anhydrous conditions, significant proportions of styrene **3** and/or 2,3,4,5,6-pentachlorostyrene (**4**) are also formed. The fact that the yield of the latter increases with reaction time, suggests its formation from styrene **3**.

With Mg, in THF, the results are unsatisfactory, acetylene **2** being formed along with ring-hydrogenated byproducts. These dechlorinations are regarded as caused by electron transfers giving radical ions, which subsequently eliminate chloride ion essentially in the manner suggested by Seiber.[17] Nevertheless, the formation of organometallic intermediates cannot be ruled out.

The UV spectrum of **2** shows a strong conjugation band around 270 nm and the characteristic secondary-band dentate structure near 300 nm (Figure 1a).[18] While the

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(1) Ballester, M.; Molinet, C. *Chem. Ind.* **1954**, 1290.

(2) Ballester, M.; Molinet, C.; Castañer, J. *J. Am. Chem. Soc.* **1960**, *82*, 4254.

(3) Fieser, L. P.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; p 1131.

(4) Ballester, M. *Bull. Soc. Chim. Fr.* **1966**, 7.

(5) Ballester, M.; Olivella, S. In "Polychloroaromatic Compounds"; Suschitzky, H., Ed.; Plenum: New York, 1974, pp 1–196 (a review).

(6) Ballester, M.; Castañer, J.; Riera, J. *An. Quim., Ser. C* **1977**, *73*, 546.

(7) Ballester, M.; Castañer, J.; Riera, J.; Parés, J. *An. Quim., Ser. C* **1980**, *76*, 157.

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(11) Ballester, M.; Castañer, J. *J. Am. Chem. Soc.* **1960**, *82*, 4259.

(12) Ballester, M.; Castañer, J.; Guardiola, E. *An. R. Soc. Esp. Fis. Quim., Ser. B* **1960**, *56*, 723.

(13) Ballester, M.; Castañer, J. *An. R. Soc. Esp. Fis. Quim., Ser. B* **1960**, *56*, 207.

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(15) Preliminary note, ref 16.

(16) Ballester, M.; Castañer, J.; Riera, J.; Tabernero, I.; Cornet, C. *Tetrahedron Lett.* **1977**, 2353.

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(18) Ballester, M.; Castañer, J.; Ibáñez, A. *Tetrahedron Lett.* **1974**, 2147.

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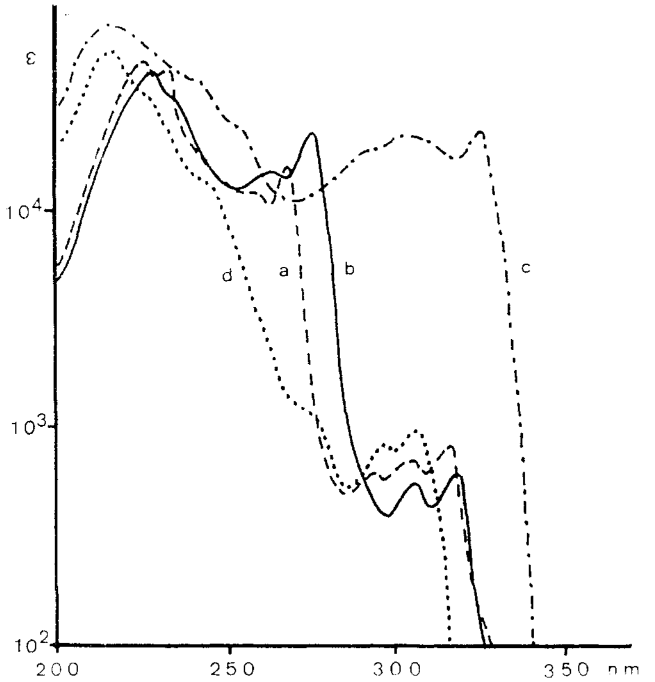


Figure 1. UV spectra of (a) *ωH*-pentachlorophenylacetylene (**2**), (b) perchlorophenylacetylene (**6**), (c) *cis*-perchloro-1,4-diphenylbutenine (**30**), and (d) perchloro-1-phenylcyclobutene (**18**).

Scheme II

$$CCl_4 \xrightarrow{h\nu} CCl_3^{\cdot} + \dot{C}l$$

$$\dot{C}l + \mathbf{6} \longrightarrow \underset{\mathbf{8}}{C_6Cl_5\dot{C}{=}CCl_2} \longrightarrow \mathbf{1}$$

Scheme III

$$\mathbf{6} \longrightarrow \underset{\mathbf{9}}{C_6Cl_5C{\equiv}C\cdot} + Cl$$

$$Cl \text{ and/or } \mathbf{9} + C_6H_{12} \longrightarrow C_6H_{11}^{\cdot}$$

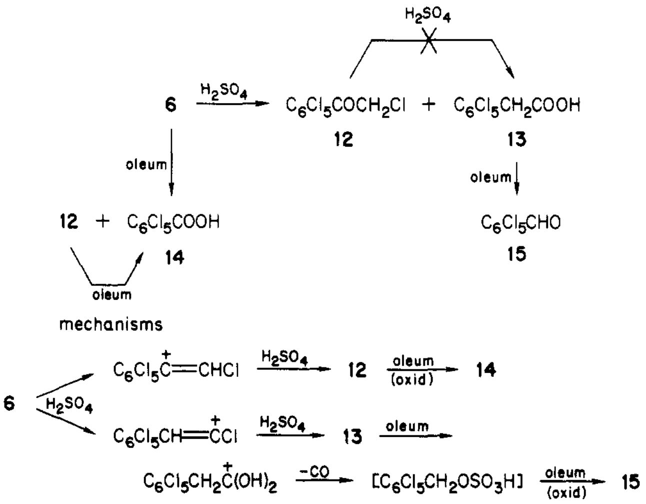
$$C_6H_{11}^{\cdot} + \mathbf{6} \longrightarrow C_6Cl_5\dot{C}{=}CClC_6H_{11}$$

$$C_6Cl_5\dot{C}{=}CClC_6H_{11} + C_6H_{12} \longrightarrow \underset{\mathbf{10}}{C_6Cl_5CH{=}CClC_6H_{11}} + C_6H_{11}^{\cdot}$$

Scheme IV

$$\mathbf{6} \xrightarrow[(HCl)]{AlCl_3,\ CH_2Cl_2} \underset{\substack{\text{cis and trans} \\ \mathbf{11}}}{C_6Cl_5CCl{=}CHCl} \xleftarrow{Cl_2} \mathbf{2}$$

Scheme V



conjugation band of perchlorostyrene is much inhibited,[19] that of acetylene **2** is not, as expected.

Perchlorophenylacetylene (6) (Scheme I). When the substitution of the terminal hydrogen of acetylene **2** is attempted by the Strauss method[20a] ($NaClO/Cl_2$, in dioxane), some perchloroacetylene **6** is formed, the major product being, however, perchloroacetophenone (**5**). Presumably, water addition is the initial step giving pentachloroacetophenone, which then undergoes exhaustive chlorination at the α carbon.

Acetylene **6** has been obtained in an excellent yield by first converting *ωH*-acetylene **2** into silver perchlorophenylacetylide (**7**). This is a remarkable silver acetylide since it is shock-resistent and withstands temperatures up to 280 °C. Acetylide **7** (in CCl_4) reacts with Cl_2 at room temperature, giving acetylene **6**. However, if the Cl_2 concentration is too high (saturation), styrene **1** is formed, even in the dark. The UV spectrum of **6** is similar to that of acetylene **2** (Figure 1b).

Additions to Perchlorophenylacetylene (6). Chlorine. Acetylene **6** reacts with Cl_2 in CCl_4, under illumination (solar or incandescent) giving excellent yields of styrene **1**. This chlorination takes place also with UV light *in the absence* of Cl_2. CCl_4 acts therefore as a chlorinating agent. This reaction may be accounted for as in Scheme II. Intermediate ethylene radical **8** cannot couple with CCl_3 (CCl_4 addition) because of steric shielding.

Cyclohexane. Under the influence of solar light, in cyclohexane, acetylene **6** gives *αH*-hexachloro-*β*-(cyclohexyl)styrene (**10**). The alternative structure for the adduct is ruled out on the grounds of steric shielding and product strain. This addition is probably initiated by homolysis of the terminal C–Cl bond of **6** affording the perchlorophenylethynyl radical (**9**). When the triple bond is flanked by two bulky ortho substituents, these type of radicals can easily be detected.[21] A reasonable chain mechanism is given in Scheme III.

Hydrogen Chloride. Acetylene **6** reacts with a refluxing solution of $AlCl_3$ in CH_2Cl_2 giving a mixture of *cis*- and *trans*-*βH*-heptachlorostyrene (**11a** and **11b**), identical with that obtained by chlorination of acetylene **2** with Cl_2 in CCl_4 (Scheme IV). In this connection, it should be mentioned that HCl is formed when refluxing a solution of $AlCl_3$ in CH_2Cl_2.

Water. Acetylene **6** reacts at 100 °C with concentrated H_2SO_4 giving *αH,αH*-hexachloroacetophenone (**12**) and some (pentachlorophenyl)acetic acid (**13**). Julia and Surzur studied this type of reaction which usually gives α-chloro ketones,[20b,22] as found here. Under the reaction conditions, ketone **12** *does not* rearrange to acid **13**. Therefore, it is reasonable to assume that the formation of ketone **12** and acid **13** takes place along different paths; i.e., that the latter does not result from a rearrangement of the former. Presumably, the initial step is protonation of the triple bond both on the α- and the ω-carbons (Scheme V, mechanisms).

When, instead of H_2SO_4, oleum is used, ketone **12** is obtained, with some pentachlorobenzoic acid (**14**), the yield of the latter increasing with temperature (from room to

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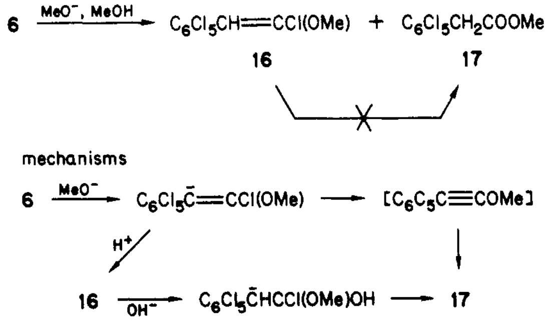
[19] Ballester, M.; Castañer, J.; Codina, J. M.; Lluch, F. *An. R. Soc. Esp. Fis. Quim., Ser. B* **1960**, *56*, 197.

[20] Delavarenne, S. Y.; Viehe, H. G. "Chemistry of Acetylenes", Dekker: New York, 1969, (a) pp 665 and 670, (b) p 693, (c) pp 693–699.

[21] Tani, H.; Tanabe, M.; Toda, F. *Chem. Ind.* **1963**, 1589.

[22] Julia, M.; Surzur, J. M. *Bull. Soc. Chim. Fr.* **1956**, 1620.

Scheme VI



100 °C). Ketone **12** is regarded as a mechanistic precursor of acid **14**, since, under the same reaction conditions, the former gives an excellent yield of the latter. It has also been found that acid **13** with oleum, at 100 °C, yields pentachlorobenzaldehyde (**15**) almost quantitatively; consequently, acid **13**—obtained with H_2SO_4—can hardly be an intermediate for acid **14**. This suggests (Scheme V) that for some reason—maybe steric—the only effectual initial proton addition to acetylene **6** *in oleum* is on the ω-carbon. The formation of aldehyde **15** from acid **13** is accounted for as shown.

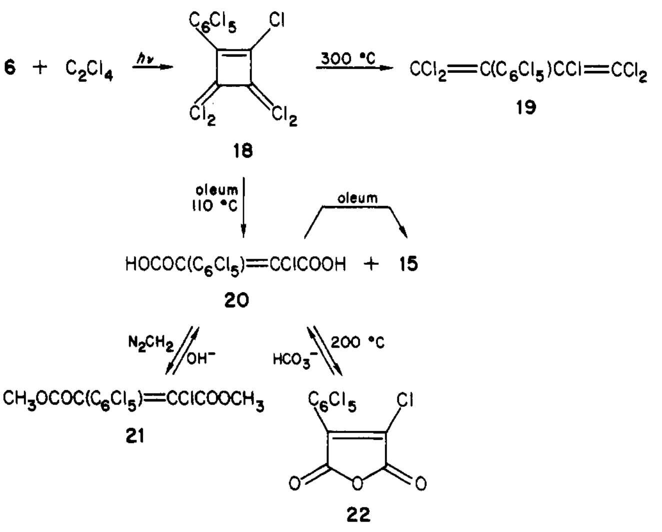
Methanol (Scheme VI). As it occurs in other ω-chloroacetylenes,[20c,22] perchloroacetylene **6** reacts with $NaOCH_3$ in CH_3OH giving a mixture of $\alpha H,\beta$-methoxyhexachlorostyrene (**16**) and methyl (pentachlorophenyl)acetate (**17**). Under the reaction conditions, **16** does not react, suggesting that it *is not* a precursor of **17**. However, under rather drastic conditions (KOH in boiling benzene) this conversion of styrene **16** can be effected. Acetylene **6** does not react with CH_3OH in the absence of $NaOCH_3$. These processes are accounted for as shown (Scheme VI, mechanisms), where the common initial step is methoxide attack to the ω carbon of **6**.

Accordingly, it has been found that yields of **16** and **17** are independent of the methoxide concentration. Therefore, there is no evidence for an initial attack of this anion to the α carbon of acetylene **6** which might lead eventually to ester **17** through rearrangement.[20b,c] This presumably does not take place in any significant extent because of steric shielding.

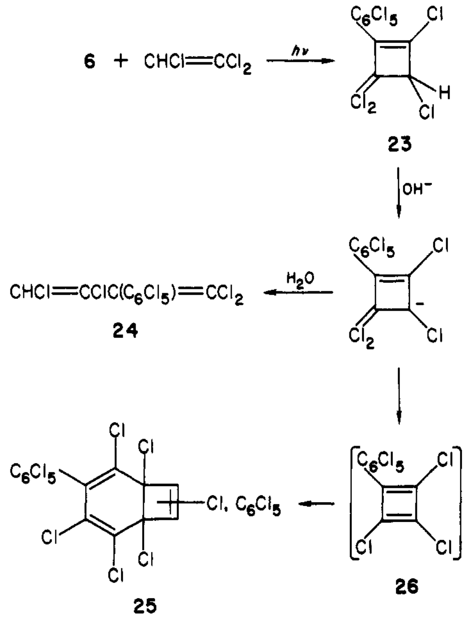
Perchloroethylene (Scheme VII). By illumination with ultraviolet light, a solution of acetylene **6** in perchloroethylene affords a good yield of perchloro-1-phenylcyclobutene (**18**). The formation of the 3-phenyl isomer is unlikely because of its steric strain. By heating **18** to about 300 °C, isomerization to perchloro-2-phenylbutadiene (**19**) takes place. When performed in the presence of copper, this isomerization occurs at lower temperatures (200 °C). The UV spectrum of **18** is, as expected, that of a resonance-inhibited styrene (Figure 1d).[19,23]

By treatment of **18** with oleum perchlorophenylmaleic acid (**20**) is obtained, along with pentachlorobenzaldehyde (**15**), the proportion of the latter increasing with time and temperature, suggesting its formation from acid **20**. Probably, the initial step of the oxidative hydrolysis of **18** consists in the formation of a carbenium ion, proceeding through perchlorophenylcyclobutenedione. In fact, Ried and Schmidt isolated chloro(phenyl)cyclobutenedione in a similar reaction.[24] Also, it is emphasized that, with oleum, perchloro-9,10-dihydrophenanthrene give first perchlorophenanthrenequinone and, finally, perchlorobiphenyl-2,2′-dicarboxylic acid.[7] Acid **20** gives its methyl ester **21** with diazomethane, and it affords the corresponding anhydride **22** by heating to about 200 °C. Both products revert to **20** by hydrolysis.

Scheme VII



Scheme VIII



Trichloroethylene (Scheme VIII). Acetylene **6** reacts with trichloroethylene, under the influence of the UV light, affording also a 1:1 adduct: 3*H*-nonachloro-1-phenylcyclobutene (**23**), as shown in Scheme VIII. This adduct, by treatment with KOH in boiling benzene, gives two products: an open-chain isomer, and a chlorocarbon $C_{20}Cl_{16}$. Since, presumably, the C_3–C_4 bond of **23** is the weakest,[25] that isomer might be 1*H*-nonachloro-3-phenylbutadiene (**24**). Accordingly, butadiene **24**, under the reaction conditions leading to its formation, affords an acetylene (IR spectrum; not identified) which could hardly be formed by dehydrochlorination from a precursor other than that shown in Scheme VIII. In this connection it is pointed out that an alternative structure for the adduct is that of the 4*H*-isomer. However, proton extraction

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(23) Ballester, M.; Castañer, J. *Anales R. Soc. Esp. Fis. Quim., Ser. B* **1970**, *65*, 487.

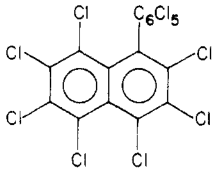
(24) Ried, W.; Schmidt, A. H. *Angew. Chem.* **1972**, *11*, 997.

(25) This bond is the weakest because both carbons are sp^3, while the other C–C bonds involve at least one sp^2 carbon and, consequently, they are stronger.

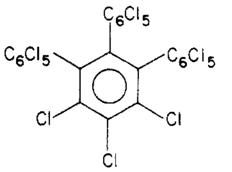
with base, to give **25**, is favored only in the 3*H*-isomer **23** because of its carbanion negative charge delocalization. Consequently, the most probable structures are those given.

As far as chlorocarbon $C_{20}Cl_{16}$, having considered carefully the work of several parties,[26] and the features of the relevant IR and UV spectra, the authors favor its being a perchlorodiphenylbicyclo[4.2.0]octa-2,4,7-triene (**25**), formed from perchloro-1-phenylcyclobutadiene (**26**).

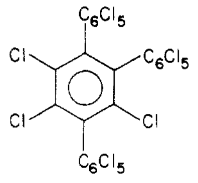
Thermal Oligomerization. Perchloroacetylene **6** oligomerizes (in perchlorobutadiene) at 210 °C, giving a mixture of two dimers and two trimers: perchloro-1-phenylnaphthalene (**27**), a perchloro dimer mp 243 °C (probably, perchloro-1,4-diphenylbutenyne (**30**)), perchloro-1,2,3-triphenylbenzene (**28**), and perchloro-1,2,4-triphenylbenzene (**29**). Chlorocarbons **27**,**28**, and **29** had been obtained by independent synthesis.[7,27]



27



28



29

$C_6Cl_5—CCl{=}CCl—C{\equiv}C—C_6Cl_5$

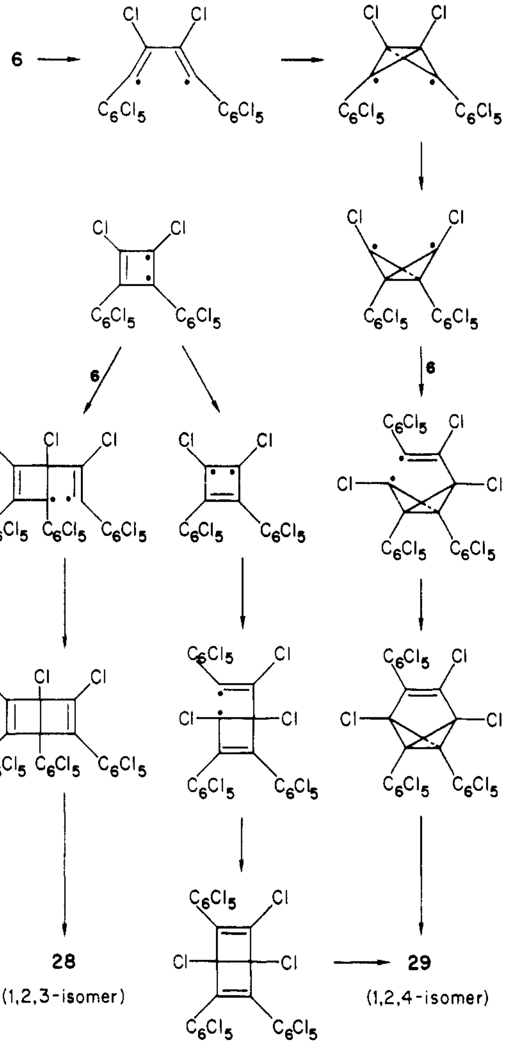
30

The oligomerization of **6** also takes place at lower temperatures (110-120 °C) in perchlorostyrene as a melting-point depressant, yielding trimers **28** and **29** and a minor proportion of a perchloro trimer mp 321 °C, but no dimers. This suggests that the temperature is not high enough for the homolysis of the terminal C–Cl bond of **6** to give ethynyl radical **9**, which would yield dimers **27** and **30**. (The oligomerization has also been carried out without a solvent, at temperatures ranging from 140 to 195 °C, the conversion yields being significantly smaller.) It looks therefore as if the dimerization and the trimerization would follow different reaction paths.

The thermal trimerization of **6** to **28** and **29**, is similar to that of *tert*-butylfluoroacetylene reported by Viehe, giving 1,2,3- and 1,2,4-tri-*tert*-butyltrifluorobenzene,[28] since both the structure of the products and the nature of the acetylene substituents (a bulky group and a halogen) are similar. Actually, they obtained first the intermediate species: a benzvalene and a "Dewar benzene". Since the trimerization here reported are rather facile, taking into account the symmetry restrictions for the relevant conversions, it is assumed that (a) all steps involved take place in a nonconcerted manner, and (b) steric repulsions involving the bulky pentachlorophenyl group are ruling factors.

Viehe assumed that the formation of the 1,2,3-triphenyl isomer takes place through a dimeric bicyclic diradical which looks like an open tetrahedrane—a structure with minimal steric repulsions among the bulky substituents since their separation is maximal. In the case of acetylene **6**, and considering the shielding provided by the pentachlorophenyl group, the sequence of Scheme IX is suggested. The dimeric bicyclic diradicals shown are, among the six valence isomers of the same general structure, the only ones that cannot afford not-found perchloro-1,3,5-triphenylbenzene. (The *tert*-butylfluorobenzene does not give the 1,3,5-isomer either.) Viehe found that the 1,2,3-isomer is formed from a Dewar benzene. Therefore, it is reasonable to assume that the formation of chlorocarbon **28** takes place as shown in the scheme, where the relevant steps avoid significant repulsions with the pentachlorophenyl group. Notice that the 1,2,4-isomer would also result from a Dewar benzene. (Only one Dewar benzene was obtained from *tert*-butylfluoroacetylene.) Scale models indicate that, because the Dewar benzenes are bent structures, no significant repulsions among the pentachlorophenyls would take place.

Scheme IX



As far as the structure of perchlorodimer mp 234 °C, its IR spectrum indicates it is a conjugated ethylene.[29] Its capability of adding chlorine (incadescent light), giving a perchlorodiphenylbutadiene, and also its UV secondary band high absorptivity and fine-structure characteristics[18] (Figure 1c) indicate it is an acetylene also. It is concluded this dimer is, as advanced, the *cis*-perchloro-1,4-di-

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(26) Roedig, A.; Helm, R. *Tetrahedron Lett.* **1969**, *26*, 2137. Roedig, A.; Bonse, J. J.; Helm, R.; Kohlhaupt, R. *Ber. Dtsch. Chem. Ges.* **1971**, *104*, 3378. Huisgen et al. *Angew. Chem.* **1964**, *3*, 83. Van Tamelen, E. E. *Angew. Chem.* **1965**, *4*, 738. Schafer, W.; Hellman, H. *Angew. Chem.* **1967**, *6*, 518. Scolt, L. T.; Jones M. *Chem. Rev.* **1972**, *72*, 181.

(27) Ballester, M. Castañer, J.; Riera, J. *An. Quim. Ser. C* **1977**, *73*, 546.

(28) Viehe, H. G.; Oth, J. F. M.; Valange, P. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 746. Viehe, H. G.; Oth, J. F. M.; Senders, J. R.; Valange, P. *Ibid.* **1964**, *3*, 746. Viehe, H. G. *Ibid.* **1964**, *3*, 755.

(29) Ballester, M.; Castañer, J.; Riera, J. *Afinidad* **1978**, *35*, 354.

phenylbutenyne (**30**). The existence of an IR ethylene stretching peak, and its being a weak one, rule out, respectively, a *trans* configuration (extremely weak peak) and the 1,2-diphenylbutenyne isomer (gem-Cl_2, medium peak).[30]

Regarding chlorocarbon mp 321 °C, which sublimes around 380 ° C, its mass spectrum shows it is a trimer of **6**; and the IR and UV spectra, that it is a highly chlorinated, unconjugated (no ethylene stretching peaks) benzene. Nevertheless, the existence of resonance-inhibited ethylene bonds cannot be ruled out.

Experimental Section

General Methods. The IR, UV–vis, ^{1}H NMR, and mass spectra have been recorded with Perkin-Elmer 457, Beckman Acta M VI, Perkin-Elmer R-12B, and AEI MS-902S spectrometers, respectively.

Since the locations of the IR peaks of perchloro organic compounds differ markedly from those of their nonchlorinated counterparts, it is useful to include them in this section.

(Pentachlorophenyl)acetylene (2). A mixture of perchlorostyrene[8] (**1**) (1.00 g), activated Zn[31] (0.50 g), and dioxane (25 mL) was refluxed (16 h; rigorous anhydrous conditions) under argon and in the dark. The resulting mixture was poured into aqueous 2 N HCl and extracted with ether. The organic layer was washed with water, dried, and evaporated to give a residue, which was purified through silica gel (hexane) and recrystallized from the same solvent yielding acetylene **2** (0.473 g; 85%), mp 180–2 °C dec (lit.[17] 180–2 °C); UV (C_6H_{12}) 224 nm, 231, 241 (sh), 258, 267, 293, 305, 317 (ϵ 48 200, 42 800, 19 000, 12 450, 15 850, 630, 750, 860); IR (KBr) 3300 (s), 2100 (w), 1370 (s), 1350 (s), 1312 (s), 1234 (s), 1130 (m), 730 (s), 710 (s), 600 (m), 649 (s), 640 (s) cm^{-1}; MS (all ^{35}Cl) 272 ($C_8HCl_5^+$); ^{1}H NMR (CCl_4) τ 6.25 (s). Anal. Calcd for C_8HCl_5: C, 35.0; H, 0.3; Cl, 64.7. Found: C, 35.3; H, 0.4; Cl, 64.8.

Perchloroacetophenone (5). A solution of acetylene **2** (0.100 g) in dioxane (50 mL) was added with stirring and in the dark to a great excess of aqueous NaOCl saturated with Cl_2. After 45 min, the reaction mixture was extracted with ether, and the organic solution was washed with water, dried, and evaporated in vacuo. The residue was submitted to TLC (silica gel; hexane) yielding perchlorophenylacetylene **6** (0.012 g; 10%) (see later), and acetophenone **5** (0.072 g; 50%), mp 92–4 °C: IR (KBr) 1750 (s), 1535 (w), 1360 (m), 1345 (s), 1315 (m), 1235 (m), 1230 (m), 1140 (m), 1040 (m), 840 (s), 820 (s), 765 (m), 665 (s), 650 (m), 580 (s), 550 (m) cm^{-1}; MS (all ^{35}Cl) 392 ($C_8Cl_8O^+$). Anal. Calcd for C_8Cl_8O: C, 24.3. Found: C, 24.2.

Silver (Pentachlorophenyl)acetylide (7). A solution of $AgNO_3$ (0.460 g; 2.71 mmol) in water (1.5 mL) was added slowly to a stirred solution of acetylene **2** (0.826 g; 3.0 mmol) in tetrahydrofuran (12.5 mL). The resulting thick mass was diluted with water and stirred for 30 min. The precipiate was filtered, washed with water and with tetrahydrofuran, and dried under vacuum (3 h; 150 °C) yielding silver salt **7** (0.834 g; 81%), mp 280 °C dec: IR (KBr) 2020 (m), 1360 (s), 1340 (s), 1310 (s), 1232 (s), 740 (s), 710 (s) cm^{-1}. Anal. Calcd for C_8Cl_5Ag: C, 25.2; Cl, 46.4. Found: C, 25.0; Cl, 46.3

Perchlorophenylacetylene (6). A diluted solution of Cl_2 in CCl_4 (100 mL) was added slowly and in the dark, to a stirred mixture of silver salt **7** (0.740 g) and CCl_4 (50 mL). After 5 min, the precipitate (AgCl) was filtered off, and the resulting solution was evaporated yielding a residue, which by purification through silica gel (hexane–CCl_4) and recrystallization from the same solvent, gave acetylene **6** (0.541 g; 90%), mp 132–5 °C: UV (C_6H_{12}) (Figure 1) 227 nm, 233 (sh), 263, 275, 306, 318 (ϵ 46 000, 37 200, 15 600, 25 300, 540, 594); IR (KBr) 2200 (w), 1380 (m), 1345 (s), 1310 (m), 1254 (m), 840 (m), 710 (s) cm^{-1}; MS (all ^{35}Cl) 306 ($C_8Cl_6^+$). Anal. Calcd for C_8Cl_6: C, 31.1; Cl, 68.9. Found: C, 31.3; Cl, 69.1.

Chlorinations of Acetylene 6. (1) A solution of acetylene **6** (0.050 g) in CCl_4 (20 mL) saturated with dry Cl_2, was irradiated (30 min) with a 300-W UV solar lamp in a Pyrex glass tube. Elimination of the volatile parts gave a residue that was purified through silica gel (hexane) and recrystallized from the same solvent yielding perchlorostyrene (**1**) (0.050 g; 81%), identified by mp and IR spectrum.[30]

(2) The preceding reaction was repeated irradiating with a 60-W incandescent lamp. The resulting product was also styrene **1** in a 74% yield.

(3) A solution of acetylene **6** (0.050 g) in CCl_4 (10 mL) was irradiated with a 300-W solar lamp as before. The resulting product was also styrene **1** in a 54.5% yield.

***αH*,β-Cyclohexylhexachlorostyrene (10).** A solution of acetylene **6** (0.075 g) in cyclohexane (15 mL) was irradiated (3 h) with a 300-W UV solar lamp at room temperature in a Pyrex glass tube. Evaporation of the volatile parts gave a residue that was purified through silica gel (hexane) and recrystallized from the same solvent yielding styrene **10** (0.057 g; 60%), mp 132–5 °C: IR (KBr) 2920 (s), 2845 (m), 1640 (w), 1625 (w), 1530 (w), 1450 (m), 1375 (s), 1360 (m), 1340 (m), 1320 (m), 1240 (m), 1120 (m), 970 (m), 885 (m), 810 (s), 805 (s), 765 (m), 720 (m), 690 (m), 650 (m), 525 (m) cm^{-1}; ^{1}H NMR (CCl_4) τ 3.77 (s, 1, ethylenic H), 8.5 (m, 11, aliphatic H). Anal. Calcd for $C_{14}H_{12}Cl_6$: C, 42.9; H, 2.8. Found: C, 43.2; H, 3.0.

***cis*- and *trans*-β*H*-Heptachlorostyrenes (11a and 11b).** (1) A slow stream of dry Cl_2 was passed (2 h) through a solution of acetylene **2** (0.100 g) in CCl_4 (20 mL). Elimination of the solvent gave a residue which was submiteed to TLC (silica gel; hexane) yielding *trans*-styrene **11b** (0.038 g; 30%), mp 106–9 °C (lit.[17] 109–10 °C), and *cis*-styrene **11a**, colorless oil (lit.[17] oil). Both compounds were identified by elemental analyses and IR, UV, and ^{1}H NMR spectra.

(2) A mixture of acetylene **6** (0.100 g), anhydrous $AlCl_3$ (1.00 g), and CH_2Cl_2 (30 mL) was refluxed (2 h) under argon. The resulting mixture was poured over aqueous 2 N HCl and extracted with ether. The organic extract was washed with water, dried, and evaporated. The residue was submitted to TLC (silica gel; hexane) yielding *trans*-styrene **11b** (0.045 g; 40%) and *cis*-styrene **11a** (0.015 g; 14%), identified as before.

Reaction of Acetylene 6 with H_2SO_4. A mixture of acetylene **6** (0.100 g) and concentrated H_2SO_4 (15 mL) was heated (100 °C; 1 h) with stirring. The resulting mixture was poured into cracked ice and extracted with ether. The ethereal layer was extracted with aqueous $NaHCO_3$, washed with water, dried, and evaporated. The residue was purified through silica gel (hexane) and recrystallized from the same solvent yielding *αH*,*αH*-hexachloroacetophenone (**12**) (0.052 g; 52%), identified by mp (141–4 °C (lit.[32] 143–4 °C)) and ^{1}H NMR:[32] IR (KBr) 2970 (w), 2930 (w), 1735 (s), 1535 (w), 1390 (s), 1375 (m), 1345 (s), 1305 (m), 1295 (s), 1220 (s), 1195 (m) 1170 (m), 1135 (s), 1040 (s), 880 (m), 785 (m), 685 (s), 635 (s), 580 (s) cm^{-1}; MS (all ^{35}Cl) 324 ($C_8H_2Cl_6O^+$). The $NaHCO_3$ extract was acidified with HCl and extracted with ether. The organic layer was dried and evaporated to give a residue which was recrystallized from ethanol yielding (pentachlorophenyl)acetic acid (**13**) (0.018 g; 18%), identified by mp (260–2 °C (lit.[33] 253–5 °C)), IR spectrum, and methylation with CH_2N_2 to the corresponding methyl ester **17** that was identified by mp (114–6 °C (lit.[33] 108–9 °C)), elemental analyses, and IR and ^{1}H NMR spectra.

Reaction of Acetylene 6 with 20% Oleum. (1) A mixture of acetylene **6** (0.100 g) and 20% oleum (15 mL) was stirred (72 h) at room temperature. The resulting mixture was poured into ice and treated as before to give acetophenone **12** (0.050 g; 48%) and pentachlorobenzoic acid (**14**) (0.010 g; 11%), identified by mp (203–5 °C (lit.[34] 208 °C)), IR spectrum, and methylation with CH_2N_2 to the corresponding methyl ester, which was identified by mp (99–100 °C (lit.[35] 97 °C)) and IR and ^{1}H NMR spectra.

(2) The preceding reaction was repeated with heating (100 °C; 1 h) yielding acetophenone **12** (25%) and benzoic acid **14** (41%).

Reaction of Acetophenone 12 with 20% Oleum. A mixture

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(30) Ballester, M.; Castañer, J. *An. R. Soc. Esp. Fis. Quim., Ser. B* **1966**, *62*, 397.

(31) The Zn was treated with 2 N HCl, washed with water, ethanol, and ether, and finally dried (50 °C, 30 min) under vacuum.

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(34) Lock, G. *Ber. Dtsch. Chem. Ges.* **1939**, *72*, 300.

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of acetophenone **12** (0.022 g) and 20% oleum (8 mL) was heated (100 °C; 1 h) with stirring. The resulting mixture was poured into ice and treated as before to give benzoic acid **14** (0.018 g; 85%).

Reaction of Acetic Acid 13 with 20% Oleum. A mixture of acid **13** (0.032 g) and 20% oleum (8 mL) was heated (100 °C; 1 h) with stirring. The resulting mixture was poured into ice and treated as before giving pentachlorobenzaldehyde (**15**) (0.026 g; 93%), mp 204–5 °C (lit.[34,36] 202.5 °C), identified by elemental analyses and IR spectrum.

Reaction of Acetylene 6 with Sodium Methoxide. A solution of $NaOCH_3$ (from Na (0.020 g; 0.83 mmol) and methanol (10 mL)) was added slowly to a refluxing solution of acetylene **6** (0.206 g; 0.66 mmol) in the same solvent (15 mL) and the reflux was continued for 15 min. The resulting mixture was poured into water and extracted with ether. The organic layer was dried and evaporated to give a residue that submitted to TLC (silica gel; hexane) yielding: (a) $\alpha H,\beta$-methoxyhexachlorostyrne (**16**) (0.053 g; 24%) [mp 95–8 °C: UV (C_6H_{12}) 213 nm, 228 (sh), 239 (sh), 277 (sh), 287 (sh), 292 (sh) (ϵ 74 300, 20 000, 10 500, 480, 420, 290); IR (KBr) 2928 (w), 2830 (w), 1647 (s), 1450 (w), 1370 (s), 1340 (s), 1305 (m), 1297 (m), 1243 (m), 1190 (m), 1090 (s), 1080 (s), 990 (s), 945 (m), 790 (s), 780 (s), 680 (s), 595 (m), 533 (m) cm^{-1}; ^1H NMR (CCl_4) τ 4.45 (s, 1, ethylenic H), 6.27 (s, 3, OCH_3). Anal. Calcd for $C_9H_4Cl_6O$: C, 31.7; H, 1.2; Cl, 62.4. Found: C, 31.9; H, 1.1; Cl, 62.7] and (b) methyl (pentachlorophenyl)acetate (**17**) (0.119 g; 52%), identified by mp (114–6 °C (lit.[33] 108–9 °C)) and IR and ^1H NMR spectra.

Perchloro-1-phenylcyclobutene (18). A solution of acetylene **6** (0.111 g) in tetrachloroethylene (7 mL) was irradiated (7 h) under argon in a sealed Pyrex glass tube with 16 UV (3000 Å) lamps. The resulting solution was evaporated to dryness, and the residue submitted to TLC (alumina; hexane) giving: (a) starting acetylene **6** (0.017 g; 15% recovery) and (b) cyclobutene **18** (0.120 g; 73%) [mp 154–7 °C: UV (C_6H_{12}) (Figure 1) 216 nm, 243 (sh), 275, 296, 306 (ϵ 56 100, 15 000, 1240, 840, 1010); IR (KBr) 1670 (w), 1530 (w), 1362 (w), 1352 (s), 1333 (s), 1255 (m), 1245 (m), 1190 (m), 1182 (m), 1142 (m), 1088 (m), 910 (m), 860 (m), 772 (s), 747 (m), 677 (m), 660 (s), 652 (s), 520 (m) cm^{-1}; MS (all ^{35}Cl) 470 ($C_{10}Cl_{10}^+$). Anal. Calcd for $C_{10}Cl_{10}$: C, 25.3; Cl, 74.7. Found: C, 25.3; Cl, 75.0.].

***3H*-Nonachloro-1-phenylcyclobutene (23).** A solution of acetylene **6** (0.350 g) in trichloroethylene (60 mL) was irradiated with UV light (5 h) as in the preceding paragraph. Evaporation of the solvent gives a residue which by TLC (silica gel; hexane) yields: (a) Starting acetylene **6** (0.028 g; 8%) and (b) a resin that by crystallization from ethanol–hexane afforded cyclobutene **23** (0.290 g; 58%), mp 80–3 °C: UV (C_6H_{12}) 215 nm, 245 (sh), 277 (sh), 297, 307 (ϵ 53 700, 13 000, 800, 830, 1000); ^1H NMR (CCl_4) τ 4.68 (s); MS (all ^{35}Cl) 436 ($C_{10}HCl_9^+$). Anal. Calcd for $C_{10}HCl_9$: C, 27.3; H, 0.2; Cl, 72.5. Found: C, 27.3; H, 0.6; Cl, 72.6.

Perchloro-2-phenylbutadiene (19). Cyclobutene **18** (0.050 g) was heated (300–15 °C min) under argon in a sealed glass tube. The resulting solid was purified through silica gel (hexane) and recrystallized from the same solvent to give butadiene **19** (0.044 g; 88%), mp 136–8 °C: UV (C_6H_{12}) 216 nm, 250 (sh), 302 (sh) (ϵ 64 200, 20 000, 1000); IR (KBr) 1585 (m), 1565 (w), 1534 (w), 1370 (m), 1350 (s), 1330 (s), 1252 (m), 1160 (m), 1110 (m), 1000 (s), 930 (s), 920 (s), 823 (s), 770 (s), 740 (m), 720 (s), 670 (s), 660 (s), 602 (s), 583 (m) cm^{-1}; MS (all ^{35}Cl) 470 ($C_{10}Cl_{10}^+$). Anal. Calcd for $C_{10}Cl_{10}$: C, 25.3; Cl, 74.7. Found: C, 25.1; Cl, 74.6.

Reaction of Cyclobutene 23 with KOH. A mixture of cyclobutene **23** (0.300 g), powdered KOH (3.0 g), and benzene (20 mL) was refluxed (24 h) with strong stirring. The resulting mixture was poured into water and extracted with ether. Acidification of the aqueous layer did not give any acidic product. The etheral layer was washed with aqueous diluted HCl and with water, dried, and evaporated to give a residue (0.243 g) that by recrystallization from hexane yielded perchlorodiphenylbicyclo-[4.2.0]octa-2,4,7-triene (**25**) (0.052 g; 19%), mp 184–6 °C: UV (C_6H_{12}) (Figure 1) 216 nm, 250 (sh), 294 (ϵ 88 000, 32 000, 12 600); IR (KBr) 1640 (m), 1590 (w), 1525 (m), 1360 (w), 1345 (s), 1330 (s), 1320 (s), 1240 (s), 1215 (m), 1172 (s), 1085 (m), 1065 (m), 985 (m), 870 (m), 795 (m), 780 (s), 740 (m), 735 (s), 670 (s), 596 (m), 540 (m), 500 (m) cm^{-1}; MS (all ^{35}Cl) 800 ($C_{20}Cl_{16}^+$). Anal. Calcd for $C_{20}Cl_{16}$: C, 29.8; Cl, 70.2. Found: C, 29.8; Cl, 70.1. Evaporation of the mother liquors gave a resin that by TLC (silica gel; hexane) yielded (a) a white solid that was recrystallized from hexane to give 1*H*-nonachloro-3-phenylbutadiene (**24**) (0.087 g; 29%) [mp 100–4 °C: UV (C_6H_{12}) 215 nm, 248 (sh), 300 (sh) (ϵ 72 200, 19 000, 950); IR (KBr) 3070 (w), 1595 (w), 1575 (m), 1530 (w), 1380 (m), 1370 (m), 1350 (s), 1330 (s), 1255 (m), 1160 (m), 1105 (m), 980 (m), 920 (s), 860 (s), 800 (m), 740 (s), 720 (s), 680 (s), 655 (s), 630 (m), 595 (m), 570 (m), 545 (m) cm^{-1}; ^1H NMR (CCl_4) τ 3.2 (s). Anal. Calcd for $C_{10}HCl_9$: C, 27.3; H, 0.2; Cl, 72.5. Found: C, 27.6; H, 0.1; Cl, 72.6] and (b) starting cyclobutene **23** (0.042 g; 14 % recovery).

Perchlorophenylmaleic Acid (20). (1) A mixture of cyclobutene **18** (0.237 g) and 20% oleum (20 mL) was heated (110 °C; 2 h) with stirring. The resulting mixture was poured into ice and extracted with ether. The organic layer was extracted with aqueous $NaHCO_3$, dried, and evaporated to give a residue that was purified through alumina (hexane) yielding starting cyclobutene **18** (0.024 g; 10% recovery). The aqueous $NaHCO_3$ layer was acidified with diluted HCl and extracted with ether. This ethereal solution was dried and evaporated to give a residue that by recrystallization from hexane–CH_2Cl_2 yielded maleic acid **20** (0.136 g; 65%), mp 155–8 °C: UV (ethanol) 213 nm, 228 (sh), 241 (sh), 287 (sh), 298 (sh) (ϵ 69 300, 25 000, 17 500, 560, 460); IR (KBr) 3640–2250 (m), 1785 (m), 1725 (s), 1709 (s), 1625 (s), 1410 (m), 1375 (m), 1350 (s), 1325 (m), 1255 (s), 1210 (s), 1070 (m), 922 (m), 795 (m), 732 (m), 690 (m), 670 (m), 610 (m) cm^{-1}; ^1H NMR (C_3D_6O) τ 1.2 (s). Anal. Calcd for $C_{10}H_2Cl_6O_4 \cdot H_2O$: C, 28.8; H, 1.0; Cl, 51.0. Found: C, 28.8; H, 1.2; Cl, 51.2.

(2) When the preceding reaction is performed with longer reaction times (3 h), or at higher temperatures (120–35 °C) the yields of acid **20** decrease (50–30%), and increasing amounts (11–44%) of pentachlorobenzaldehyde (**15**) are isolated.

Dimethyl Perchlorophenylmaleate (21). An excess of ethereal solution of CH_2N_2 was added to a solution of acid **20** (0.079 g) in ether. The resulting solution was evaporated and the residue was purified through alumina (hexane) to give ester **21** (0.076 g; 90%), mp 113–5 °C: UV (C_6H_{12}) 212 nm, 227 (sh), 238 (sh), 288 (sh), 300 (ϵ 75 600, 30 000, 19 000, 680, 580); IR (KBr) 3000 (w), 2945 (w), 2840 (w), 1755 (s), 1730 (s), 1628 (m), 1435 (s), 1370 (m), 1344 (s), 1320 (m), 1260 (s), 1075 (s), 1015 (s), 995 (s), 915 (m), 872 (m), 828 (m), 785 (s), 768 (m), 753 (m), 720 (m), 685 (m), 640 (m), 610 (m), 578 (m) cm^{-1}; ^1H NMR ($CDCl_3$) τ 5.93 (s, 1), 6.17 (s, 1). Anal. Calcd for $C_{12}H_6Cl_6O_4$: C, 33.7; H, 1.4; Cl, 49.8. Found: C, 33.6; H, 1.3; Cl, 49.7.

Perchlorophenylmaleic Anhydride (22). Acid **20** (0.050 g) was heated at 200 °C (1 h). Anhydride **22** (0.025 g) sublimed as crystals mp 127–9 °C: UV (C_6H_{12}) 213 nm, 229 (sh), 241 (sh), 288 (sh), 300 (sh) (ϵ 81 300, 35 000, 21 000, 600, 500); IR (KBr) 1865 (w), 1793 (s), 1782 (s), 1650 (w), 1625 (w), 1530 (w), 1370 (m), 1352 (s), 1337 (m), 1268 (m), 1245 (s), 1240 (s), 1110 (m), 915 (s), 800 (m), 780 (m), 730 (m), 680 (m), 625 (m) cm^{-1}. Anal. Calcd for $C_{10}Cl_6O_3$: C, 31.5; Cl, 55.8. Found: C, 31.6; Cl, 56.0. The residue was recrystallized from hexane to give more anhydride **22** (0.010 g), the total yield being 73%.

Hydrolysis of Ester 21. A solution of ester **21** (0.043 g) in dioxane (15 mL) was treated with aqueous 1 M NaOH (15 mL) with stirring (15 min) at room temperature. The resulting mass was poured into water, extracted with ether (no neutral fraction extracted), acidified with aqueous HCl, and extracted again with ether. The organic layer was washed with water, dried, and evaporated. The residue was recrystallized from hexane–CH_2Cl_2 to give acid **20** (0.036 g; 85%).

Hydrolysis of Anhydride 22. A solution of anhydride **22** (0.050 g) in ether (20 mL) was treated with aqueous $NaHCO_3$ (30 mL) with stirring (15 min) at room temperature, and decanted. The ethereal layer was dried and evaporated; no residue was found. The aqueous layer was acidified with aqueous HCl and extracted with ether. The organic extract was treated as in the preceding hydrolysis yielding acid **20** (0.050 g; 92%).

Attempted Dechlorinations of Cyclobutene 18. (1) A mixture of cyclobutene **18** (0.039 g), $SnCl_2 \cdot 2H_2O$ (0.473 g), and dioxane (25 mL) was refluxed (8 h) with stirring. The resulting mixture was poured into water and extracted with ether. The

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(36) Lock, G. *Ber. Dtsch. Chem. Ges.* **1933**, *66*, 1527.

ethereal solution was washed with aqueous HCl and with water, dried, and evaporated. The residue was starting cyclobutene **18** (0.037 g; 95% recovery).

(2) A mixture of cyclobutene **18** (0.025 g), NaI (0.200 g), and acetic acid (10 mL) was heated on a steam bath (30 min). The resulting mixture was poured into water and extracted with ether. The ethereal solution was washed with aqueous $NaHCO_3$ and with water, dried, and evaporated. The residue was starting cyclobutene **18** (0.024 g; 96% recovery).

(3) A mixture of cyclobutene **18** (0.020 g) and powdered Cu (0.20 g) was heated (200 °C; 15 min) under argon, and the resulting mass was extracted with ether. The organic extract was purified through alumina (hexane) to give butadiene **19** (0.016 g; 80%).

Thermal Treatments of Acetylene 6. (1) At 210 °C in Perchlorobutadiene. A solution of acetylene **6** (0.300 g) in perchlorobutadiene (50 mL) was heated (210 °C; 1 h) under argon. Elimination of the solvent (0.5 mmHg; 90 °C) yielded a residue which by digestion with boiling hexane and TLC (silica gel; hexane) afforded: (a) starting acetylene **6** (0.038 g; 13% recovery), (b) *cis*-perchloro-1,4-diphenylbutenine (**30**) (0.060 g; 20%) [mp 231–4 °C: UV (C_6H_{12}) 216 nm, 225 (sh), 240 (sh), 253 (sh), 293 (sh), 305, 310 (sh), 325 (ϵ 74 000, 62 000, 41 000, 25 000, 19 500, 22 800, 21 000, 23 300); IR (KBr) 1565 (w), 1525 (w), 1405 (m), 1365 (m), 1345 (s), 1335 (s), 1308 (m), 1240 (m), 975 (s), 930 (s), 870 (m), 760 (m), 720 (s), 710 (s), 655 (m), 642 (m), 628 (m), 592 (s), 492 (m) cm^{-1}; MS (all ^{35}Cl) 612 ($C_{16}Cl_{12}^+$). Anal. Calcd for $C_{16}Cl_{12}$: C, 31.1; Cl, 68.9. Found: C, 31.3; Cl, 68.9], (c) perchloro-1-phenylnaphthalene (**27**) (0.040 g; 13%), mp 274–8 °C (lit.[7] 276–8 °C), (d) perchloro-1,2,4-triphenylbenzene (**29**) (0.030 g; 10%), mp 305–9 °C (lit.[6] 306–8 °C), and (e) perchloro-1,2,3-triphenylbenzene (**28**) (0.040 g; 13%), mp 293–6 °C (lit.[6] 293–6 °C). The structure of compounds **27**, **28** and **29** has been confirmed by IR and UV spectroscopy.[6,7]

(2) **At 190–5 °C.** Acetylene **6** (1.544 g) was heated (190–5 °C; 30 min) under argon. The resulting mass, by column chromatography (alumina; hexane), yielded: (a) a yellowish product that by recrystallizations from hexane–ether gave perchloro-1-phenylnaphthalene (**27**) (0.379 g; 25%), mp 274–8 °C and (b) a brown resin that by sublimation (250 °C; 0.5 mmHg) and TLC (silica gel; hexane) gave perchloro-1,2,4-triphenylbenzene (**29**) (0.116 g; 7.5%), mp 305–9 °C and perchloro-1,2,3-triphenylbenzene (**28**) (0.287 g; 19%), mp 293–6 °C.

(3) **At 140–5 °C.** Acetylene **6** (0.100 g) was heated (140–5 °C; 7 h) under argon. The resulting mass was treated as in (2) giving naphthalene **27** (0.010 g; 10%), 1,2,4-triphenylbenzene **29** (0.019 g; 19%) and 1,2,3-triphenylbenzene **28** (0.023 g; 23%).

(4) **At 110–20 °C in Perchlorostyrene.** A mixture of acetylene **6** (0.265 g) and perchlorostyrene (**1**) (0.285 g) as the solvent was heated (110–20 °C; 24 h) under argon. The resulting mass was treated as in (2) giving styrene **1** (0.271 g; 95% recovery), 1,2,4-triphenylbenzene **29** (0.067 g; 25%), 1,2,3-triphenylbenzene **28** (0.167 g; 63%), and an isomeric $C_{24}Cl_{18}$ (0.021 g; 8%), mp 319–21 °C: UV (C_6H_{12}) 212 nm, 224 (sh), 294 (ϵ 128 000, 91 800, 3470); IR (KBr) 1535 (w), 1380 (w), 1362 (s), 1340 (s), 1320 (s), 1142 (m), 1117 (m), 1070 (m), 910 (m), 882 (m), 870 (m), 780 (m), 775 (m), 762 (m), 730 (s), 717 (s), 695 (s), 680 (m), 660 (s), 650 (m), 640 (m), 620 (m), 580 (m), 565 (m), 555 (m) cm^{-1}; MS (all ^{35}Cl) 918 ($C_{24}Cl_{18}^+$).

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Registry No. **1**, 29082-74-4; **2**, 37123-28-7; **5**, 100571-02-6; **6**, 52598-45-5; **7**, 65350-47-2; **10**, 100571-03-7; **11a**, 29086-39-3; **11b**, 29086-38-2; **12**, 22551-88-8; **13**, 100571-04-8; **14**, 1012-84-6; **15**, 19635-52-0; **16**, 100571-05-9; **17**, 100571-06-0; **18**, 100571-07-1; **19**, 100571-08-2; **20**, 100571-09-3; **21**, 100571-10-6; **22**, 100571-11-7; **23**, 100571-12-8; **24**, 100571-13-9; **25**, 100571-15-1; **27**, 77302-45-5; **28**, 70994-48-8; **29**, 71140-77-7; **30**, 100571-14-0; $Cl_2C{=}CCl_2$, 127-18-4; $Cl_2C{=}CHCl$, 79-01-6; $SnCl_2$, 7772-99-8; Cu, 7440-50-8; NaI, 7681-82-5; cyclohexane, 110-82-7; perchlorobutadiene, 87-68-3.

Arynic Condensation of Ketone Enolates. 17.[1] New General Access to Benzocyclobutene Derivatives

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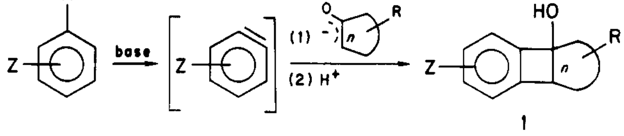
Arynic condensation of 1,2-diketone monoketal enolates appeared to be a very simple way to synthesize benzocyclobutene derivatives. X-ray diffraction and ^1H NMR spectra allowed us to determine the structure of the new compounds and to propose a mechanism concerning these condensations. Finally, during this work we devised a new and easily performed two-step synthesis of 1,2-diketones.

The abundant literature dealing with benzocyclobutene derivatives shows how attractive these compounds are.[2] They constitute an important family of starting materials for the obtention of a large variety of polycyclic compounds. Moreover their syntheses very often constitute an interesting challenge, and a convenient access to these structures is always desirable.[3]

Scheme I



For some years, our laboratory has been studying the synthesis and the chemical transformation of benzocyclobutene derivatives.

Our interest increased when we discovered that benzocyclobutenols **1** (Scheme I) had anticonvulsant properties[4]

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