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On Assembling Polychlorinated Aromatic Hydrocarbons from Carbon Tetrachloride via Dichlorocarbene Intermediary by a Solvothermal Reaction: A Reaction Pattern from Carbene−Ylide Interconversion

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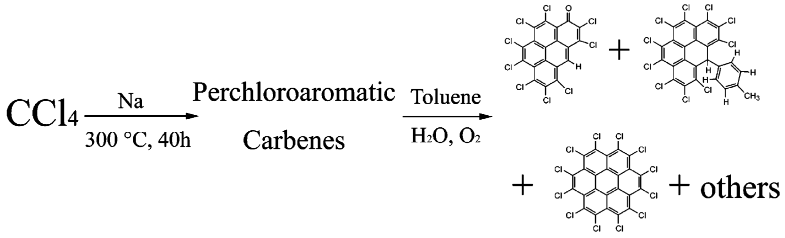

The forced one-electron reduction of carbon tetrachloride with sodium in a sealed steel vessel is shown to have a narrow window of conditions to arrest the reaction at the polychlorinated aromatic hydrocarbons (PCAHs), as well as to prevent the reaction from proceeding all the way to the final stage of graphite and other carbon solids. The intermediates are quenched with toluene or benzene to give electrophilic substitution products and with water to give a quinomethine as the major product. The product pattern leads us to propose the carbene, perchlorobenzo[*c,d*]pyren-6-ylidene, or its reversible dimer as the major intermediate among others, that survives the severe conditions until coming into contact with these nucleophiles. Mainly from aromatic resonance stabilization, the carbene is proposed to have a delocalized singlet state analogous to a ylide electronic structure and, thus, undergoes observed ionic reactions instead of typical carbene reactions. This work serves as a mechanistic link on the structural evolution of carbon networks between molecular chemistry and nanomaterial chemistry.

Introduction

The formation of a C−C bond through one electron-reductive coupling of haloalkanes with alkali metals, commonly known as the Wurtz reaction,[1] has been in use for a long time but rarely applied in more complex organic synthesis owing to many limitations, among them the severity of the reducing agent, alkali metals. When alkali metals (or their mixtures) react with polyhalogenated alkanes the process may be modified; for example, the reactions with CCl_4 are known to generate dichlorocarbene[2,3] ($:CCl_2$) as a reactive intermediate, accumulation of which may cause sudden and violent reactions. For this reason, chemists have been warned to be cautious in handling any mixture of polyhaloalkanes and alkali metals in laboratories[3,4] until recent years, when in a quick succession it was reported that such reactions could be safely performed without an explosion in a sealed steel reactor.[5−8]

This modification used a higher pressure/temperature than those reactions in ambient conditions, and often in the presence of metal salts as catalysts, to strip chlorine

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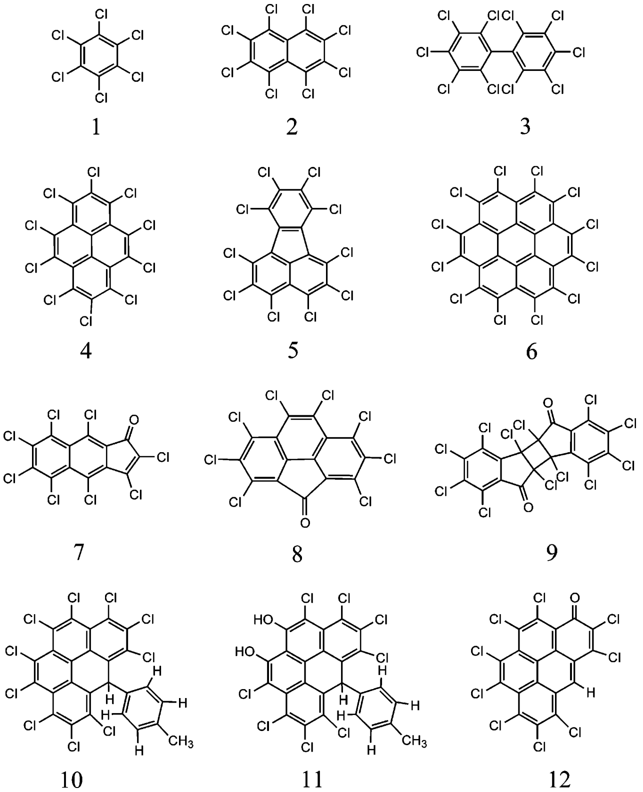

FIGURE 1. PCAHs isolated from the products of solvothermal reaction of CCl_4 with Na.

in an orderly fashion from polychlorohydrocarbons, that is a reaction under solvothermal conditions.[5] This technique has been successfully used to prepare nanoscale carbon solid materials; for example, diamond powders from CCl_4,[5] carbon nanotubes from hexachlorobenzene (**1** in Figure 1)[6a,b] and tetrachloroethylene,[6c] carbon onions from hexachloropentadiene,[7] and hollow spherical graphite from **1**.[8] Allied reactions using perfluorinated hydrocarbons or CCl_4 to synthesize various carbon nanotructures (e.g., nanotubes) have also been reported.[9]

We have long-standing interests in the fabrication of fullerenes and allied carbon materials.[10−12] One technique is high voltage electric discharge in liquid[10] or vaporized[11] chloroform and CCl_4; in such a process we have isolated perchlorinated aromatic hydrocarbons (PCAHs) that can be construed as building blocks for fullerenes and also identified a trace of C_{50} derivative,[12] as well as C_{60} and C_{70}. Under the solvothermal conditions as described above, it was indeed puzzling that the reaction was either nil or gave completely black carbon materials even when the 1:1 mole ratio of CCl_4 to Na was used (see below). Unfortunately, in the existing reports on carbon materials,[5−9] researchers basically regard this reaction as a routine technique with arbitrary intermediates and pay scarce attention to the molecular transformation and structural details for integrating carbon to complex molecules. They[5−9] also point to the fact that the reaction is very sensitive to the small changes of conditions such as temperature, duration, diluents, etc. As the intermediate PCAHs would provide key information to assign rational mechanisms of carbon material formations, the search of the reaction conditions and analysis of the intermediates were undertaken. This paper describes the separation and isolation of some PCAHs with molecular weight (MW) <700 and the proposal of reactive intermediates that can be used to examine the formation mechanism in the early to middle stage for solid carbon materials. While complexity of the product pattern may discourage synthetic chemists, at this early stage of development the proposal of major intermediates is the first attempt in the field; it opens up the first entry to clarify mechanistic links to molecular and nanomaterial chemistry.

Results

Optimization of the Reaction Conditions. In a Teflon-lined stainless steel reactor a mixture of carbon tetrachloride (0.26 mol) and sodium (0.13 mol) gave no significant reaction at 220 °C for 40 h either in the absence or presence of $CoCl_2$, $NiCl_2$, $CuCl_2$, and/or $FeCl_3$ as catalysts. Subsequently, exploration was carried out in a bare stainless steel vessel at this reactant ratio. When the temperature was set at 300 °C a good amount of toluene-soluble substances, identified as highly polychlorinated aromatic hydrocarbons (PCAHs), and some insoluble black amorphous carbon (mainly graphite) were obtained. The latter black carbon materials increased rapidly at the expenses of PCAHs at 400 °C and totally dominated the crude product at 800 °C, in addition to a small amount of iron carbide, as shown by X-ray diffraction (XRD) analysis. At 300 °C and a CCl_4/Na mole ratio of 0.26:0.13 (i.e., 2:1), PCAHs were obtained copiously and largely consisted of those with molecular weight below 700. While with the mole ratio at 1:1 the crude product was almost completely graphite, with the ratio at 6:1 PCAHs decreased drastically and consisted of primarily small polychloroaromatic molecules (MW 200−400).

At 400 °C, the reaction was finished in less than 12 h giving much black materials. At 300 °C, Na was not totally consumed in <30 h. Thus, the standard conditions for the present investigation were set at the reaction of CCl_4 (0.26 mol) and Na (0.13 mol) in a stainless steel reactor at 300 °C for 40 h. The conditions led to complete consumption of Na and gave off a small amount of yellow fume that was assumed to be the chlorine gas when reactor was opened. The reproducibility of the reaction under optimal conditions was well established. Owing to corrosion, the reactor was changed every few runs. As this exothermic reaction builds up a moderately high pressure and temperature during heating, the reactor must be protected inside an appropriate shield; upon completion the reactor can be opened safely at the room temperature.

Product Analysis and Isolation. The exposed reaction mixture was immediately quenched with toluene to afford products which were separated into the toluene (or ethylbenzene) soluble part and insoluble materials; the former contained the intermediates for the formation of the latter and was the target of the present investiga-

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tion. As the toluene solution contains some 50 odd PCAHs, some of which are in trace amounts and/or high molecular weight with limited solubility in various solvents, it is a challenge to perform analysis, isolation, and identification. For this, high-performance liquid chromatography (HPLC) coupled with ultraviolet spectroscopy (UV) and/or mass spectrometry (MS) is a powerful and efficient tool at the present stage.[13] This research group, over many years' experiences dealing with allied reactions and related PCAHs, has established efficient methods and know-hows in these separation techniques. Detailed HPLC−UV/MS procedures for the separation and identification of the present PCAH series were described in the Ph.D. thesis of Y.P.;[14] the method was developed on the basis of the principle and practice in dealing with other PCAH series.[15] The toluene solution was investigated with this analytical system to give an HPLC chromatogram as shown in Figure S1 (see the Supporting Information). It must be understood that peak heights (or areas) are good indicators of abundance, but are not strictly proportional to the concentrations, i.e., corresponding yields. Those well-defined chromatographic peaks were examined with HPLC−UV and/or HPLC−MS; the latter MS spectra generally gave distinct molecular ion peaks whose chlorine isotope distribution pattern[16] was utilized to judge the number of chlorine and, in turn, to compute the molecular formula. Among the structures of the products, perchlorobenzene **1**,[17] perchloronaphthalene **2**,[18] perchlorobiphenyl **3**,[19] perchloropyrene **4**,[20] and perchlorofluoranthene **5**[21] (see Figure 1) have been previously characterized. In the present experiment, they were readily identified by co-injection HPLC and confirmed when isolated (vide infra) by direct spectral comparisons with authentic samples available in our group. For the mechanistic studies, early stage intermediates must be identified to provide a reaction pattern, i.e., major peaks of PCAHs with the MW range 500−700 should be identified. Larger molecules of MW >700 were produced in low yields and, together with their solubility problems, not amenable to isolation.

The crude product from the toluene solution was sublimed at 120−160 °C and then up to 200 °C to remove mostly **1**, but in the latter range, in addition small amounts of **2**−**5**. HPLC−MS and co-injection with authentic samples were used to identify these PCAHs. The remaining solid was chromatographed repeatedly on a neutral alumina column using cyclohexane as the eluent to afford pure samples of **2**−**4** and 1,2,3,4,4b,4c,6,7,8,9,9b,9c-dodecachloro-4b,4c,9b,9c-tetrahydrocyclobuta[1,2-*a*;3,4-a′]diindene-5,10-dione $C_{18}Cl_{12}O_2$ (**9**),[22] 6-(*p*-tolyl)-6*H*-1,2,3,4,5,7,8,9,10,11-decachlorobenzo[*cd*]pyrene $C_{26}Cl_{10}H_8$ (**10**),[23] and 6-(*p*-tolyl)-6*H*-1,11-dihydroxy-2,3,4,5,7,8,9,10-octachlorobenzo[*cd*]pyrene $C_{26}Cl_8H_{10}O_2$ (**11**) as shown in Figure 1. An ethylbenzene soluble extract was also chromatographed in the similar way to afford perchlorocoronene ($C_{24}Cl_{12}$, **6**),[24] and perchlorobenzo[*f*]indenone $C_{13}Cl_8O$ (**7**), and 1,2,3,5,6,7,8,9-octachlorocyclopenta[*def*]phenanthren-4-one $C_{15}Cl_8O$ (**8**).[25]

Repeated column chromatography caused much loss of materials in each run due to irreversible adsorption and band overlaps and demanded a large outlay of time and solvents for good separations. To circumvent these drawbacks, a combined column and HPLC process was also developed as an alternative. That is, an ethylbenzene extractive was chromatographed on an alumina column but eluted with toluene to give four blocks of mixtures. The first fraction was recrystallized many times to give perchlorofluoranthene **5**. The last two fractions were worked up by preparative HPLC; 6*H*-1,2,4,5,7,8,9,10,11-nonachlorobenzo[*cd*]pyrene-3-one $C_{19}Cl_9HO$ (**12**) was obtained from the third fraction. In addition, three higher molecular weight PCAHs, among others, were also obtained in milligram scales just enough to record their MS, infrared (IR), and/or UV spectra; this group included $C_{25}Cl_{10}O_2$ and two isomers of $C_{26}Cl_7H_5O$ and was not investigated further.

The MS, UV, and IR spectra of these PCAHs were recorded. X-ray crystallography was employed to identify the structures of **5**, **6**, and **8**−**12**; details of the X-ray structure of **8**−**10** have been reported.[22,23,25] However, owing to availability and solubility of these PCAHs, ^1H and ^{13}C NMR spectra were successfully obtained only with **10**, which was isolated in the largest amount. These physical parameters are discussed in conjunction with X-ray structures below. It should be noted that owing to tedious and inefficient isolation procedures, product yields could not be evaluated with reliability; some isolated weights are given in the Experimental Section. On the basis of the isolations, **10**−**12** were major and **5**−**9** minor products; the major products added up to a 6% yield (75 mg) on the basis of individual calculations.

X-ray Structures and Properties. Owing to the large steric volume of chlorine atoms, these PCAHs have degrees of molecular strains that cause skeletal distortions, which should greatly affect their physical properties. Thus detailed molecular shapes by X-ray crystallography were obtained wherever good grade crystals could be obtained. As a detailed description requires a large space, in this paper only relevant structures and parameters will be given to facilitate discussion. The X-ray structures of both **5** and **6** are in record, the former was analyzed again as $(C_{16}Cl_{10})_2/CS_2$, the crystal obtained in recrystallization from carbon disulfide (see Figure S2 in the Supporting Information). Both structures show

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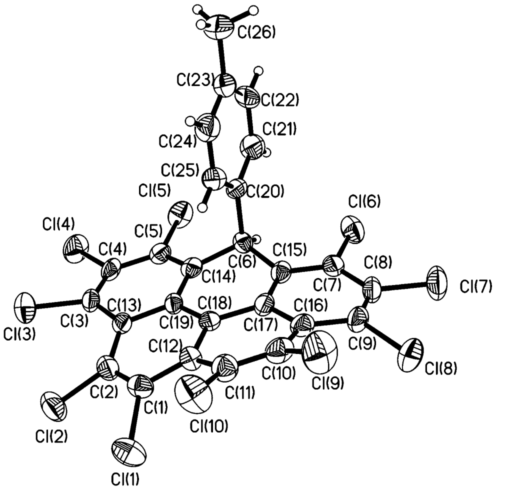

FIGURE 2. Crystal structure of **10**.

severe twist from coplanarity arising from chlorine overcrowding; the former arising from opposing chlorines at the two 1,4-angular positions, and the latter from parallel 1,3-C−Cl bonds at the six *peri*-positions. As the result, the latter molecular surface has three humps around the periphery. **9** has a twisted cyclobutane ring with all-cis chlorine orientations; two fused indanone rings avoid each other in space (Figure S3 in the Supporting Information). Compound **8** has a planar surface despite two 1,3 *peri*-interactions as shown in Figure S4 (Supporting Information) that are obviously much relieved due to tightening of the pentadienone ring. Both **7** and **8** show typical pentadienone IR band at 1721 and 1731 cm^{-1}, respectively. The structure of **7** is tentatively assigned on the basis of MS, and its IR and UV spectra that are distinctly different from those of perchlorofluorenone[26] and perchlorophenalenone,[27] and calculations using the semiempirical PM3 method.[28a] In addition, density-functional theory (B3LYP/6-31G)[28b] calculations prove the relative energy of **7** (−19.5553 kJ/mol) is much lower than its isomers benzo[*e*]indenone (0 kJ/mol) and benzo[*g*]indenone (−10.4900 kJ/mol). Were the X-ray structure of **7** available, it should show significant molecular distortion due to a double *peri*-interaction (i.e., three nearly parallel 1,3-C−Cl bonds).

While PCAHs **10**−**12** share the same PCAH skeleton, their X-ray structures are quite different from the small difference in substitution patterns. In both **10** and **11** (Figure 2 and Figure S5, Supporting Information) the toluene ring is forced into a nearly perpendicular orientation with respect to the PCAH ring and does not exert significant effects on PCAH steric-wise. Major product **10** has the most distorted PCAH surface followed by **12** (Figure S6, Supporting Information) and then **11**. The measured deviation from the average PCAH plane is 0.1844, 0.1352, and 0.0719 Å, respectively, and the maximum (minimum) angles of distorted six-membered ring planes against each other in the PCAH surface are 21.2° (2.8°), 14.5° (4.2°), and 11.3° (2.0°), respectively. The magnitude of deviations shows the size of surface humps in these three PCAHs and **5**−**6** and becomes clearer when compared with the planar structure of **8** in Figure S4 (Supporting Information). It follows that two hydroxyl groups in **11** relieve such crowding significantly probably owing to intramolecular hydrogen bonding, but the quinoid (IR band at 1650 cm^{-1}) moiety in **12** did not alleviate the steric crowding very much. All of them show pertinent IR, UV, and MS spectra. Compound **10** shows the pertinent ^1H NMR signals (see the Experimental Section) and 16 ^{13}C NMR signals that require a plane of symmetry cutting across the C-6.[29] As the X-ray structure (Figure 2) shows the lack of such a plane, the molecule must be undergoing fast (i.e., faster than the NMR time scale) wagging motion of the PCAH surface in the solution phase at the cavity temperature. Such fast conformational exchanges create an average PCAH plane with the plane of symmetry that can afford the observed 16 ^{13}C NMR signals.[16]

Miscellaneous Reaction Conditions. To trace the source of oxygen atoms present in some PCAHs, the standard reaction conditions were maintained but the quenching process was modified to see the effects on the product pattern. First of all, the reaction mixture upon opening was immediately quenched with either water or benzene instead of toluene. In both cases the resulted HPLC spectra were completely different and devoid of **10** and **11** as expected. In the former spectrum a very large peak of **12** was recorded and was isolated as the major product. In the latter case, a peak corresponding to $C_{25}Cl_{10}H_6$ (**10′**, i.e., **10** where tolyl = phenyl) was detected through HPLC−MS, although the intensity was not as prominent as that of **10** from toluene quenching. The implication was unmistakable that at the end of the solvothermal reaction an intermediate accumulated and reacted with toluene to give **10**−**11** and benzene to **10′** and also with water to give **12**.

Separately, a reaction, including the weighing of Na, was prepared inside a drybox under nitrogen and sealed. The reaction was performed and worked up in the usual way to be quenched by toluene; the toluene solution was HPLC analyzed to show the complete absence of peaks corresponding to **7**, **8**, and **9** and a much-reduced intensity of the peak for **11**. But significantly, the peak corresponding to **12**, though relatively small, was still present. Thus oxygen atoms in **7**−**9** and **11** must be derived from oxygen in the air entered into the reaction at the beginning, and that in **12** must not be from the air but from adventitious moisture upon the opening of the reaction vessel.

Discussion

The published[5−9] as well as present results show that the solvothermal reaction of Na (or K) with CCl_4 (or other polychlorocarbon) in a closed vessel readily strips chlorine atoms sequentially and integrates single carbon units to reach a wide range of carbon materials. Our exploration indicates that the reaction of Na with CCl_4 has a narrow window of conditions by which the reaction can be

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SCHEME 1

$$\mathrm{CCl_4} \xrightarrow{\mathrm{Na^{\cdot}}} \mathrm{CCl_4^{\cdot -}\,Na^+} \xrightarrow{\mathrm{-NaCl}} \mathrm{CCl_3^{\cdot}} \xrightarrow{\mathrm{Na}} \mathrm{CCl_3^{-}Na^+}$$

$$\xrightarrow{\mathrm{-NaCl}} \mathrm{:CCl_2} \xrightarrow{\mathrm{2\ :CCl_2}} \mathrm{Cl_2C{=}CCl_2} \xrightarrow{\mathrm{2Na}} \mathrm{ClC{\equiv}CCl}$$

arrested at the PCAH level without going down to carbon materials. At 300 °C in a closed reactor both reactants must be a superheated fluid under a certain high pressure. Under such extreme conditions, its reaction mechanism can only be speculated on the basis of the product pattern upon quenching. The stepwise one electron reduction of CCl_4 by Na under such conditions appears to proceed slowly to give the observed product pattern, which is different from that of an open electric arc discharge in CCl_4 and chloroform.[10,11] The latter is initiated by high-voltage (10 kV) electron capture that produces PCAHs containing five-membered rings (e.g., perchlorinated acenaphthene,[21b,30] fluoranthene,[21] and corannulene[10,31]); those carbon skeletons with built-in five-membered rings are generally accepted precursors as building blocks for fullerenes.[32,33] The present reaction produces PCAH precursors for mostly graphite except a small amount of perchlorofluoranthene; its early stage reactions could be formally written (among other possibilities) as in Scheme 1 according to the accepted one-electron reduction mechanism.[2] Thus, we interpret that dichlorocarbene and tetrachloroethene are the basic building blocks for the observed PCAHs. This interpretation shares the same mechanistic pathway, at least at the initial stage, with the former arc discharge reaction,[10,11] and supported by the formation of some small PCAHs, such as **1** and **2**, in common. At the pressure and temperature under the reaction conditions, tetrachloroethene is more likely to undergo thermal [2 + 2]- and [2 + 2 + 2]-type cycloadditions[34] more rapidly than to undergo reductive chlorine elimination. Dichloroacetylene is less likely an intermediate, but that cannot be proven at this stage. Another possibility is that in the present reaction dichlorocarbene may react with anion $NaCCl_3$ faster than dimerize by itself; this remains to be studied.

While under such severe reaction conditions an extensive scatter of products as observed is unavoidable, good yields of **10** and its congeners **11** and **12** are indeed surprising and remarkable. These three products share the same PCAH frame that suggests the major pathway for this reaction; namely, under the conditions the reaction coalesces to an intermediate that must be persistent owing to structural reasons until contacting with benzenes or water to undergo irreversible reactions. As shown in Scheme 2, we propose perchlorobenzo[*c,d*]pyren-6-ylidene in its singlet state[2,35] **14a** as the reactive species for the intermediate and the corresponding *gem*-dichloro derivative **13** as a precursor; for all probability the latter is rapidly reduced by Na to **14** aided by the steric crowding[26] at the CCl_2 moiety (at C-6) and has only a fleeting lifetime. A carbene with the sp^2 hybridization for the reactive center in the condensed aromatic system is deduced rationally on the basis of products **10**–**12** isolated upon quenching and also prevalent reductive dechlorination by Na. The singlet electronic state **14a** is rationalized to be the lowest (or very close to the lowest) ground state as the intermediate mainly in analogy to well-established aromatic carbene intermediates published in the literature.[2,35–37] First, the electron pair is placed in the sp^2 orbital which has a lower energy than the empty *p*-orbital that creates aromatic resonance stabilization from 18 $(4n + 2)$ π-electrons in a circular carbenium ion configuration.[38] This is in good analogy to extensively studied case of cycloheptatrienylidene and diphenylcyclopropenylidene;[35–37,39] in particular, the former was shown conclusively by MNDO computations,[40–43] IR spectroscopy,[38a] and trapping experiments[44] to have a singlet-state electronic configurations in the ground state, though the structure varies with a complex pattern.[40,41] Second, suitably located chlorine substituents[43] in the periphery can donate electron pairs through conjugation to the vacant carbene *p*-orbital to stabilize **14a**, as it is a well-established fact that heteroatom electron pairs[36,45] can lower the singlet state energy to the extent of gaining ground singlet state, e.g., in xanthilidene[46] and dimethoxyfluorenylidene.[47] Finally, the electron pair (negative charge) in the sp^2 orbital is shielded from steric crowding of the both *peri*-positions that prevent its access to a attacking species, except probably to a small proton.

Compound **14b** with the electron pair localized in the *p*-orbital, owing to contradiction against the reasons state above, should have a higher energy and can scarcely contribute to the structure of the intermediate. It must be added that in the case of 2,5-cyclohexadienon-4-ylidene and allied cases, this electronic configuration definitely assume importance from a reason of negative charge

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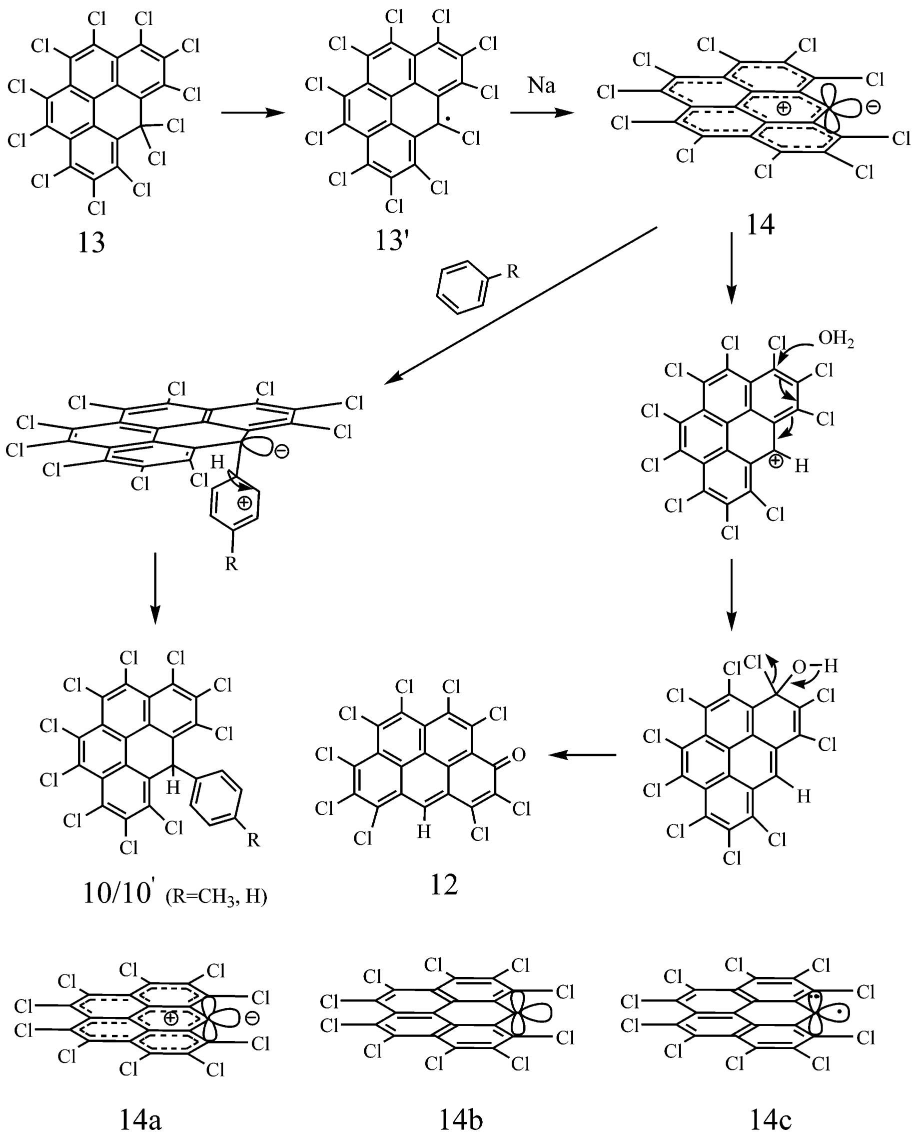
SCHEME 2



delocalization.[48] Whereas in general, alkyl and phenyl carbenes have a triplet diradical in the ground state,[2,35] in the present case triplet diradical **14c** is believed to have a comparable or even higher energy than **14a** on the reasons as discussed above. While attempted calculations of the energy difference between **14a** and **14c** have not been successful, we speculate that the singlet–triplet energy split is, in analogy to those above aromatic carbenes,[35–37,39,48bc] fairly small in the order of few kilocalories either ways. Thus, under the reaction conditions, there is no agent to intercept carbene **14a** except a small amount of intruding oxygen from the beginning that allows its survival. The related oxygenation will be discussed later. The concept of resonance stabilized carbenes is similar to that described for heteroatom electron pair stabilized singlet carbenes[49] appeared while this is in preparation; both have ylide electronic structures. Alternatively, carbene **14a** may survive under the conditions as its dimeric form with a severely twisted C=C bond in analogy to perchloro-9,9-bifluorenylidene;[50] the weak C=C bond allow the dimer to reversibly generate **14a** under the thermal conditions. Even under severe steric crowding from *peri*-bis-chloro interactions, we may envisage certain kind of dimeric association through a long bonding. The discussion of other carbenes (see below) can share similar alternative possibilities.

Having proposed carbene **14** as the intermediate, the observed reaction pattern must be discussed. The benzyl derivatives corresponding to **10** and **11** have not been identified in isolable quantities among complex products, although small amounts may have escaped the detection. This indicates that carbene **14** has feeble (or lacks) singlet insertion and triplet radical reactivity. Those singlet carbenes cited above also tend to be more facile in addition than insertion, and do not insert into the α-CH bonds of tetrahydrofuran.[2] While the access for spectroscopic examinations of the intermediate is beyond reality at this stage, singlet carbene **14a** can be perceived as a

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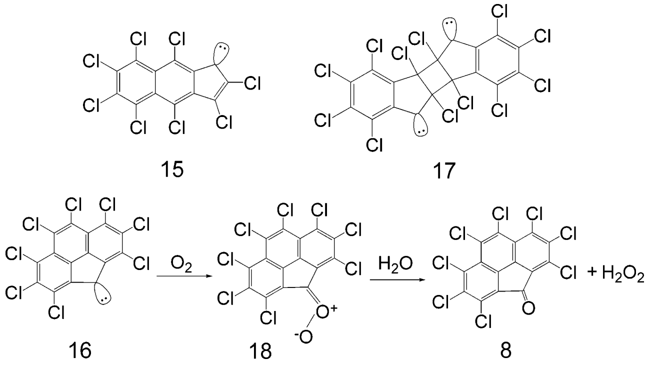
SCHEME 3



zwitterion (or ylide) of the localized electron pair in the sp^2 σ-orbital and an extensively delocalized positive charge in the p-orbitals over the aromatic frame.[36,37] The reaction of such a ylide must reflect its electronic structure; with water it should be most facile by initial protonation and with a benzene ring by the π-complex formation. The former protonation is in agreement with nucleophilic reactivity of cycloheptatrienyliden[51] and allied carbenes;[36,37,45] this leads to **12** after elimination of HCl. The latter π-complex should collapse by an electrophilic bond formation in the aromatic substitution pattern leading to **10** and **11**. These reaction pathways must be energetically the lowest and should be lower than the activation energy required for insertion or hydrogen abstraction for this type of delocalized and hindered carbenes.[39,45] Thus, we propose here carbene **14** that does not undertake typical carbene reactions but preferentially does ordinary ylide ionic reactions in the ground state as the intermediate. Together with those delocalized singlet carbenes,[39,45,51a] they may be classified as anomalous carbenes.

Triplet carbenes are known to be trapped by oxygen with a diffusion-controlled rate to form a carbonyl oxide (or ylide),[36,52] known as the Criegee's ozonolysis intermediate from the original proposal,[53] which reacts with water to give a carbonyl compound and H_2O_2; for example, **18** in Scheme 3. Noting that the carbonyl oxygen atom in minor PCAHs **7**−**9** is derived from oxygen in the intruding air, we suggest that these ketones are derived from the corresponding carbenes **15**−**17** (i.e., structural analogues to **14**); **15**−**17**, in turn, should come from the corresponding vicinal dichloro-derivatives as logical precursors through reductive dechlorination by Na (see Scheme 1) and probably exist as their dimeric forms in the reaction solution (vide supra).[50] These perchloro aromatic carbenes **15**−**17**, regardless of their electronic configuration in the ground state, should have a small singlet−triplet energy split[54] from the reasons discussed above; even if **15**−**17** possess a ground singlet state, they can cross over the energy surface at the high reaction temperature to react as a triplet with oxygen.[55,56] As their carbene center is not severely hindered, they are rapidly scavenged by floating oxygen. In Scheme 3, the transformation of **16** via **18** to **8** is used as the model to illustrate the oxidation process to ketonic PCAHs **7**−**9**. It is also expected that **14a** may react with oxygen in the same way after surface crossing, albeit more slowly from steric crowding at the carbene center, to afford the corresponding ketone. We did find a medium peak having $C_{19}Cl_{10}O$ in the crude toluene extract (see Figure S1, Supporting Information), but could not isolate this compound, presumably it was difficult to come out of column. Finally, we assume that a carbene similar to **14** but with two OH substituents at the 1,11-position must be the corresponding precursor to **11**. However, we have no simple mechanism to incorporate an oxygen molecule into the particular 1,3-position.

Going back to Figure 1, while PCAHs **1**−**3** are common to solvothermal reactions of CCl_4, and their structures are too small and early in the process to tell the story in the skeletal integration process, those of **4**, **6**, **10**−**12** suggest that they (or their precursors) are the intermediates for graphite.[8] PCAHs **5** and **8** are most likely the precursors to perchlorocorannulene,[10,11,31] which incorporates a five-membered ring to cause curving of molecular surfaces and has been assumed to be a precursor of carbon onions and fullerenes.[7,12,32,33] Their low yields suggest that such final carbon materials must be minor products. We have difficulty to fit ketones **7** and **9** into these reaction schemes and suspect that they are dead alleys in the reaction. On the basis of the known pericyclic reactions,[57] there should be more than one acceptable mechanistic pathway that can be proposed for the sequential integration of building blocks, :CCl_2 and $Cl_2C{=}CCl_2$, to give PCAHs in Figure 1. At this stage, with limited information it is not profitable to go into deeper mechanistic discussions.

Finally, it is necessary to comment on a small amount of what appears to be a yellow chlorine gas observed when the vessel is opened. It is envisaged that chlorine could be generated by thermolysis of suitable perchloro intermediates at the point when all Na was consumed. It is known that perchlorodiphenylmethane undergoes rapid thermal dissociation to form a chlorine atom and stabilized radical;[26] many stabilized (or persistent) radicals from steric reasons and extensive delocalization[58] from thermal dissociation are well documented. In view of observed severe distortion in the vicinity at C-6 in **10**−**11** (see Figure 2), *gem*-dichloro precursor **13** must be just as (or even more) seriously crowded sterically and a good candidate to undergo homolysis at 300 °C to a stabilized radical **13′** that should afford chlorine. There is no information to suggest the thermolytic fate of **13′** in the product pattern; at 300 °C many reactions may occur to relieve strains due to the double 1,3-peri interaction of three parallel C−Cl bonds in **13′**. We may venture to speculate the gaining of greater stabilization in addition

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to relieve strains may help further homolysis of the remaining C_6-Cl to give **14**.

In conclusion, the forced one-electron reduction of CCl_4 with Na under the solvothermal reaction produces PCAH intermediates that are on its way to be integrated into graphite and allied carbon solids. Under the controlled conditions as defined, perchlorobenzo[*c,d*]pyrene-6-yl, carbene (**14**) is deduced to be the major intermediate that can be quenched with benzenes and water to afford corresponding products **10**−**12**. Mainly from aromatic resonance stabilization carbene **14** is proposed to have a delocalized singlet state analogous to an ylide electronic structure and should undergo observed ionic reactions instead of prototype carbene reactions. Under the reaction conditions, **14** exists as a stable carbene−ylide resonance hybrid or alternatively stabilized as a reversible carbene dimer. Whereas the product pattern is complex, the integration process of one carbon unit to **14** provides a critical insight into mechanisms of carbon solid formations. The reaction should and could be improved to be a stepping stone to nanomaterial chemistry.

Experimental Section

Forced Reaction of Carbon Tetrachloride with Sodium. A clean piece of freshly cut sodium (ca. 3 g) and CCl_4 (25 mL) were placed in a stainless steel autoclave (40 mL capacity). Sodium stored in paraffin was first cleaned on a filter paper and skinned to remove the covering sodium oxide. The sealed autoclave was heated in an oven to 300 °C for 40 h. This was allowed to cool to the room temperature for uncapping which was immediately followed by the addition of toluene (30 mL). A small puff of yellow fume that was assumed to be the chlorine gas gave off when the reactor was opened. The mixture quenched by toluene was allowed to stand in the air for evaporation; the remaining crude product was washed several times with water to leach out NaCl. The filtered solid was dried at 100 °C and sublimed at 160−200 °C to give a white crystalline mixture (150 mg) of perchlorobenzene and some **2** and **3**. The remaining solid was divided into two equal parts of organic mixtures (10 g total). The first part was triturated with toluene (20 mL) and filtered through a 0.45 μm pore filter to remove carbon black and other inorganic materials. The second part was treated similarly with ethylbenzene (20 mL). The toluene and ethylbenzene extracts were analyzed with HPLC−UV/MS; a HPLC spectrum of the toluene extract is shown in Figure S1 (Supporting Information).

The products were isolated by preparative chromatography, and the weight yields (here and all others) were calculated on the basis of the total crude. An aliquot (2 mL) of the toluene extract was taken up on an alumina column and eluted with cyclohexane to afford impure fractions. These impure fractions each containing a major component were rechromatographed in the similar mode repeatedly to obtain small amounts of pure products. After a series of chromatography, the isolated weight, normalized to the total crude, in a typical experiment were **2** (20 mg), **3** (15 mg), **4** (2 mg), **10** (40 mg), **9** (1 mg), and **11** (15 mg). One-half of the ethylbenzene extract (10 mL) was chromatographed on an alumina column and cyclohexane in the similar method as above to afford, among others, **6** (1 mg), **8** (1 mg), and **7** (10 mg) in normalized weights.

The other half of the ethylbenzene extract was taken up in an alumina column and eluted with toluene to afford four impure fractions **A**−**D** in the order of elution. Fraction **A** was recrystallized from cyclohexane three times to afford **5** (6 mg). The fractions **C** and **D** were separated with a preparative HPLC on an ODS column (ECONO-PREP C18 column, 250 mm in length and 21.2 mm in diameter) employing methanol/toluene/water (75:25:5 volume ratio) as the mobile phase through repeat operations. From fraction **C**, **12** (20 mg) was isolated. Also, from fraction **C** and **D** few milligrams each of $C_{25}Cl_{10}O_2$ and two $C_{26}Cl_7OH_5$ isomers were obtained; their IR, UV, and MS spectral data as well as some details of isolating each member of these products were recorded in the thesis of Y.P.[14]

X-ray Crystallographic Analysis. X-ray quality single crystals of these PCAHs (except **7**) were obtained by crystallization from the cyclohexane and/or toluene solution, except **5** which afforded the CS_2 complex in good crystalline form. The X-ray structural analyses data were collected at 298 K on a SMART 1000 CCD diffractometer (for compounds **6** and **9**−**12**) or an Enraf-Nonius CAD4 diffractometer (for compounds **3**, **5**, and **8**) equipped with a Mo-target X-ray tube ($\lambda = 0.71073$ Å). The structure was resolved with direct methods and refined with full-matrix least-squares using the SHELX-97[59] software package.

The deviation from the average PCAH plane was measured as the distance of the farthest carbon atom perpendicular to the average PCAH plane, which was calculated by a least-squares method[59] from pertinent PCAH carbons coordinates. In Figure 2 for **10**, for example, the average PCAH plane was computed from the 19 PCAH carbon atoms (i.e., C1−C19); whereas the deviation from the PCAH plane was the vertical distance between C6 and the PCAH plane; C6 was farthest form the PCAH plane than others. The angle of distorted six-membered ring planes was determined by the dihedral angle between two neighbor six-membered ring planes sharing a common bond.

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Supporting Information Available: Description of starting materials and analytical methods; analytical and spectroscopic data for compounds **5-12**; typical HPLC−UV chromatogram of the toluene-soluble products and ORTEP drawing for the structures of **5-CS₂**, **8**, **9**, **11**, and **12**. X-ray crystallographic structural data (CIF) for compounds **11 and 12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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