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Nucleophilic Substitution in Hexachlorocyclopentadiene

S.A.Ismailov

Nucleophilic substitution reactions occurring when hexachlorocyclopentadiene is acted upon by various bases are surveyed and discussed critically. Certain characteristic features of reactions of this type are demonstrated.
The bibliography includes 133 references.

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I. INTRODUCTION

The "chlorine accumulator",[1] namely hexachlorocyclopentadiene (HCCPD), which is widely used in organic syntheses, has been frequently the subject of review articles[2-5] and a monograph, the first in the periodical literature, devoted to the chemistry of this and related compounds, has been published recently.[6] HCCPD is a unique synthon for perchlorinated skeletal compounds. It was also the first representative of dienes with "reversed electronic character" in relation to the dienophile in the diene synthesis[8,9] and hence permitted the treatment of the mechanism of the Diels–Alder reaction at a still deeper level. By virtue of the ready formation of the aromatic pentachlorocyclopentadienyl anion, HCCPD has become an irreplaceable object for the development of the concept of "X-philic reactions" in organic chemistry.[10]

The diene adducts obtained on its basis are used as fireproofing agents, which make polymers incombustible[11-20] and most of them exhibit pronounced insecticidal,[21-26] fungicidal[27-30] and herbicidal properties.[31-41] Some of these pesticides, such as aldrin, dildrin, etc., are used in the national economy.[42] However, in recent years the range of applications of these compounds has been sharply curtailed and in some countries their use has been prohibited,[43] since they suffer from a significant disadvantage—their natural degradation in nature is slow and it involves the formation of toxic perchlorinated compounds.[44]

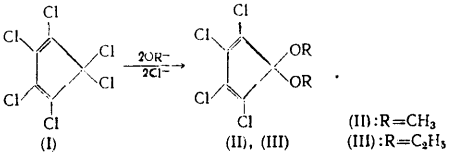
It is believed that one of the possible solutions of this problem is the modification of HCCPD [45] and its diene adducts[46] by substituting some of the chlorine atoms by functional groups. Despite the existing exceptions,[46,48] the substitution of chlorine atoms by alkoxy-groups by the S_N1 mechanism in the HCCPD adducts is usually difficult owing to the high energy of the sp^2-hybridised carbonium anion at the bridgehead of the norbornene skeleton;[49-51] direct substitution also cannot be achieved because of steric hindrance in the attack by the nucleophile from the rear of the bridging carbon atom. Since HCCPD contains two allylic chlorine atoms and four vinyl chlorine atoms and these can be readily exchanged for different anions, the most acceptable and the simplest method of modification involves nucleophilic substitution in the HCCPD itself and not in its adduct. The present review is devoted to such reactions.

Analysis of the literature data demonstrates certain characteristic features of these reactions compared with nucleophilic substitution in other halogenocarbons.

On the other hand, the diene adducts obtained from substituted perchlorocyclopentadienes are of interest, because, by virtue of the presence of the readily hydrolysable ketal group, they are key compounds for the synthesis of useful substances with specified steric structures, which are otherwise difficult to obtain.[52-54]

II. SUBSTITUTION ON TREATMENT WITH SATURATED AND UNSATURATED ALCOHOLS (MONOHYDRIC AND DIHYDRIC), MONOTHIOLS AND DITHIOLS, AND MONOAMINES AND DIAMINES

A number of studies have been devoted to the nucleophilic substitution of chlorine atoms in HCCPD by saturated monoalkoxide anions.[55-59] It was first shown in 1947 [60] that the interaction of HCCPD (I) with KOH in ethanol at room temperature leads to 1,2,3,4-tetrachloro-5,5-diethoxycyclopentadiene (III) in a high yield. Other 5,5-dialkoxy-1,2,3,4-tetrachlorocyclopentadines can be obtained analogously:[55]



(I) (II), (III) (II): R=CH_3 (III): R=C_2H_5

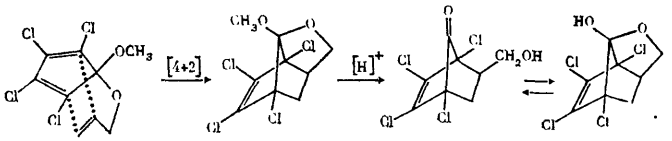
The dienes (II) and (III) are stable compounds which readily enter into the Diels–Alder reaction with various dienophiles, like HCCPD. The stability of these dienes is determined by the presence of the ketal group,[61,62] which ensures the partial shielding of the tetrachlorocyclopentadiene ring and hence hinders the dimerisation process. This is confirmed by the striking tendency of 1,2,3,4-tetrachlorocyclopentadienone,[55] 1,2,3,4-tetrachlorocyclopentadiene,[63] and 1,2,3,4,5-pentachlorocyclopentadiene[64,65] to dimerise via the Diels–Alder reaction.

The high reactivity of HCCPD in nucleophilic substitution has aroused special interest. This compound should apparently be inert with respect to the action of a nucleophile, since direct substitution of the allylic chlorine atoms is difficult owing to steric hindrance to the attack by the nucleophile. Substitution via the ionisation mechanism is impossible, since it requires the formation of the antiaromatic pentadienyl cation, which is destabilised by the overall inductive effect of the five chlorine atoms; this carbonium ion is stable only at low temperature.[66]

Kinetic studies of the interaction between HCCPD and a methanol solution of KOH showed[67] that the reaction is of second order (of first order with respect to HCCPD and the base). Consequently, the rate of reaction is determined by the first bimolecular stage, while a second chlorine atom is substituted in the rapid stage. The authors emphasise that the reaction of HCCPD with an equimolar amount of KOH in

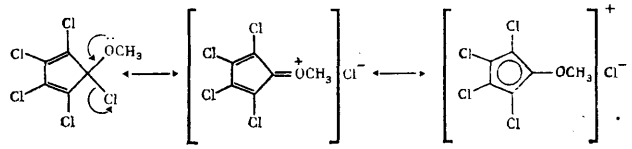
methanol gives rise exclusively to compound (II) both with refluxing and in the cold, approximately 50% of the HCCPD being recovered. It was not possible to detect the intermediate—the monomethoxy-derivative (IV).

However, a study has been recently published[68] in which it was possible to demonstrate indirectly the formation of 1,2,3,4,5-pentachloro-5-monomethoxycyclopentadiene (IV). Treatment of the unpurified diene (II), obtained by the method of McBee et al.,[7] with potassium allylate in allyl alcohol at 50 °C in the course of 4 h led to the isolation of the pure colourless diene (II) and ~3% of compound (VI):



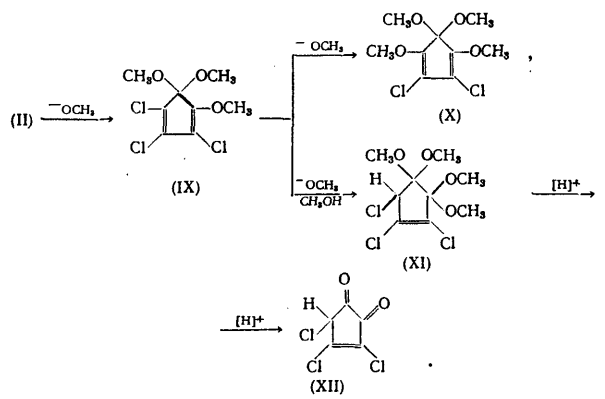
(V) (VI) (VII) (VIII)

The structures of compounds (VI), (VII), and (VIII) obtained were established by spectroscopic methods and by chemical reactions. The intermediate triene (V) can be formed only from the monomethoxy-derivative (IV) when the latter is treated with potassium allylate. The yellow colour of the diene (II) obtained by the method of McBee et al.[67] has been explained by the presence of a small amount of the monomethoxy-derivative (IV) as an admixture, to which the following resonance structures were ascribed:[67]



(IV)

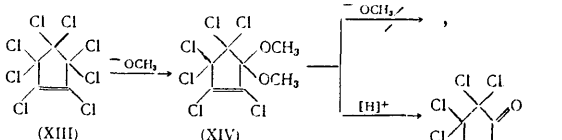
The subsequent reaction of the diene (II) with the methoxide anion is claimed[67] to afford the trimethoxy-compound (IX), which undergoes two simultaneous reactions after brief treatment with the methoxide anion:



(IX) (X) (XI) (XII)

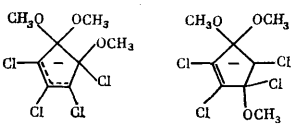
Trichlorotetramethoxycyclopentene (XI), whose structures was inferred from hydrolysis with formation of a compound allegedly identical with the known 3,4,5-trichlorocyclopent-3-ene-1,2-dione (XII),[69] was believed to be the main reaction product under these conditions. However, the position of the OCH_3 group in compounds (IX), (X), (XI), and (XII) was established incorrectly (see below). The tentative diene structure (IX) and (X) of the compound were proved by involving them in the diene condensation with maleic anhydride and also by the IR and UV spectroscopy.

Bimolecular nucleophilic substitution of chlorine in HCCPD could be achieved, in principle, in three positions—at the 1-, 2-, and 5-carbon atoms. Direct substitution of the allylic chlorine atom in the 5-position via the S_N2 mechanism is impossible. The inability of compound (XIV) to react further with the methoxide anion is consistent with this hypothesis:[67]



(XIII) (XIV) (XV)

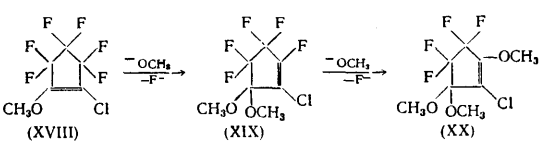
If substitution takes place at one of the two allylic centres in compound (XIII), then the second centre should also react on the reasonable assumption that the dimethoxymethylene group in the product (XIV) does not deactivate the remaining allylic dichloromethylene group. This fact shows that the vinyl position is the centre of attack. The possibility of vinyl attack in these systems follows from the reactivity of the dienes (II) and (IX). The preferred direction of the attack on one of the two centres of the vinyl component of the cyclopentadiene ring has been explained as follows:[67] in reactions of this type, the affinity for nucleophiles characteristic of the substrate undergoing substituion is more important than the polarisability of the nucleofuge. The rate of formation of new bonds depends on the relative stability of the charged intermediate, which is the driving force of the reaction. The increase in the stability of the intermediate anion can be achieved by the charge distribution among several bonds. Hence, in the case of compound (II) there should be two types of vinyl chlorine atoms undergoing substitution and one of two charged intermediates, (XVI) and (XVII), should be formed:



(XVI) (XVII)

The above considerations give preference to the formation of the structure (XVI), but, contrary to expectation, the structure (XVII) is produced, as we shall see below.

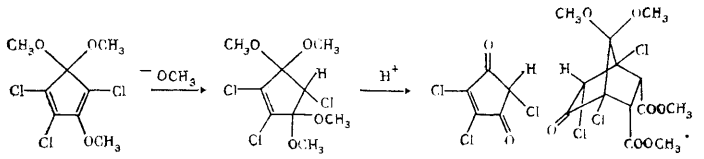
Information about the allylic shift of the double bond and the vinyl attack in these reactions has been obtained[67] with the aid of the reactions of the model compound (XVIII):



(XVIII) (XIX) (XX)

By adding slowly a methanolic solution of alkali to the product (XVIII), compound (XIX) was obtained, whose structure indicates the allylic migration of the double bond on substitution. The subsequent addition of the methoxide ion leads to the product (XX). The formation of compound (XX) indicates vinyl substitution in the 1-position in the cyclopentene ring without involving the chlorine atom, which has

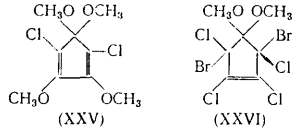
been explained[67] by the relatively high reactivity of the vinyl fluorine atom compared with the vinyl chlorine atom. However, in order to make sure of the reliability of the results, it would be useful to employ the chlorinated analogue of compound (XVIII). This type of substitution in compound (II) should lead to the formation of the structure (XXI) and not (IX). Indeed, when the above reaction was carried out, the authors[70,71] showed that the methoxide anion attacks the carbon atom in the 2-position in the cyclopentadiene ring and compound (XXI) was isolated under these conditions, its structure being established by its conversion into compound (XXII) by treatment with the methoxide anion and acid hydrolysis of this product the corresponding diketone (XXIII):



(XXI) (XXII) (XXIII) (XXIV)

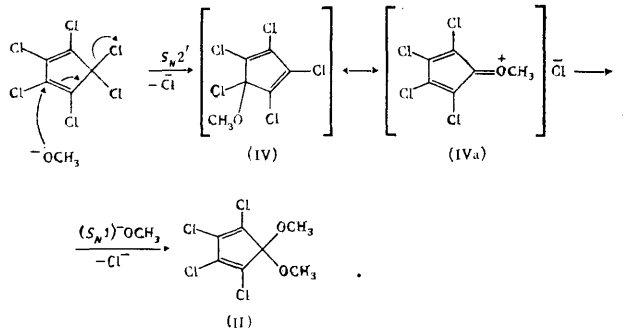
The mistake by McBee et al.[67] was that they attributed the structure of compound (XII) to the ketone (XXIII) obtained. The physicochemical constants of these isomeric ketones are fortuitously identical. The structure of compound (XXI) was demonstrated by diene condensation with dimethyl maleate and the hydrolysis of the product to the corresponding ketone (XXIV). From these data, the structure (XXV) and not (X) can be attributed to the second diene obtained by McBee et al.[67] The structure (XXI) had been attributed to the product as early as 1965 [70] and was then confirmed in 1973;[71] this phenomenon was called the "anomalous effect".

It is noteworthy that the direction of attack by the nucleophile on the vinyl component of the cyclopentadiene ring probably depends on the relative electron density at the carbon atom, i.e. the anion should attack the carbon atom at which the electron density is lowest. Unfortunately, there are no quantitative data concerning this hypothesis for such a system. The vigorous interaction of the diene (II) with electrophilic bromine, leading to the 1,4-adduct (XXVI), may indicate the validity of the above hypothesis.[55]



(XXV) (XXVI)

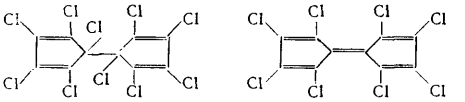
Thus the following mechanism has been put forward[71] based on the kinetic data for the reaction of HCCPD with the methoxide anion[67] and the stereochemical reactions of the products:[70,71]



(IV) (IVa) (II)

As can be seen from this scheme, regardless of the way in which the first chlorine atom in HCPPD undergoes bimolecular substitution, the rate of the second stage of the reaction will be appreciably higher, since the intermediate—pentachloro-5-methoxycyclopentadiene (IV)—undergoes unimolecular exchange of the allylic chlorine via the carbonium ion (IVa), in which the methoxy-group ensures additional resonance stabilisation. On the other hand, the exceptional sensitivity of α-chloro-ethers to bases is well known.[67,69]

It is of interest that compounds (XXVII) and (XXVIII), obtained by the reaction of HCCPD and Cu_2Cl_2, are exceptionally inert with respect to the action of alkoxides,[72,73] which has been explained by steric and resonance effects. These compounds also fail to undergo the diene condensation with dienophiles of different types.

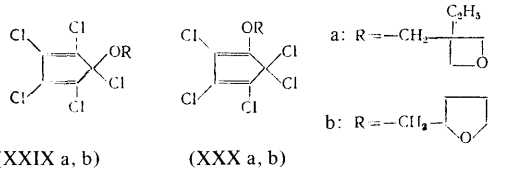


(XXVII) (XXVIII)

The reaction of HCCPD even with more bulky nucleophiles, such as isopropyl, t-butyl,[57] and benzyl alcohols,[74] etc. affords 5,5-disubstituted products. The reactions with phenol[75] and thiophenol[76] give rise to the monosubstituted as well as the disubstituted products.

A study[77] in which the reaction involving the substitution of chlorine in HCCPD by 2-ethylhexoxide was considered and it was shown that it proceeds exclusively with formation of a monosubstituted product—pentachlorocyclopentadienyl 2-ethylhexyl ether—is of considerable interest.

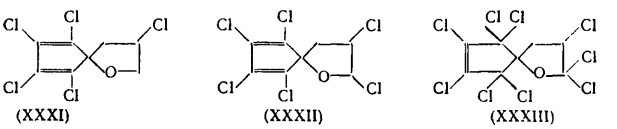
It has also been established[78] that the nucleophilic substitution reaction of HCCPD with two bulky nucleophiles—3-ethyl-3-hydroxymethyloxetan and tetrahydrofurfuryl alcohol—leads simultaneously to two isomeric monosubstituted compounds (XXI) and (XXX) without the formation of disubstituted products:



(XXIX a, b) (XXX a, b)

The authors emphasise that both products interact vigorously with methanol in the presence of acid catalysts and that R is then substituted by CH_3. However, the reaction mechanism is not described. The absence of *gem*-disubstituted products in this reaction has been explained by steric factors generated by the nucleophiles themselves. The structures of the compounds obtained were established by the analysis of their IR spectra and of the Diels–Alder adducts obtained with various dienophiles. The formation of the isomer (XXX) is probably associated with the 1,5-migration of the chlorine atom in the cyclopentadiene ring.

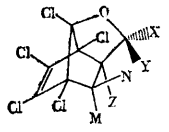
The nucleophilic substitution of a chlorine atom in HCCPD by unsaturated anions has its characteristic features. It has been claimed[79] that, when the allylate anion reacts with HCCPD, the monosubstituted adduct (XXXI) is formed.



(XXXI) (XXXII) (XXXIII)

A patent[80] describes a study of the chlorination reaction of this compound, which allegedly yielded compounds (XXXII) and (XXXIII), but the structure (XXXI) attributed to the initial compound is incorrect.

Sometime later, an analogous reaction was carried out with monomethyl-substituted allyl alcohols and it was discovered that it takes place readily at 25–30 °C in aprotic solvents with formation of the oxatricyclononene skeleton: [81]

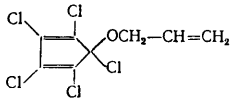


(XXXIV)

where X, Y, Z, M, and N are various alkyl and aromatic groups.

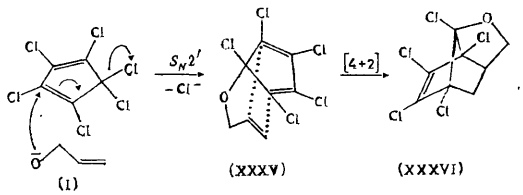
It is noteworthy that the author[81] does not reject the formation of compound (XXXI) in the case of allyl alcohols; an attempt was made to account for the cyclisation reaction in the formation of compound (XXXIV) by the electronic and structural effects generated by the alkyl or aryl substituents.

In 1969 the reaction with allyl alcohol was repeated[82] under fairly severe conditions (100–150 °C) and the structure (XXXV) was attributed to the product thus obtained:



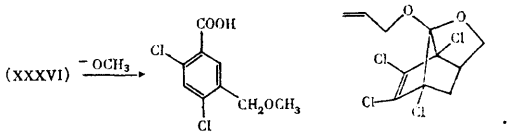
(XXXV)

However, spectroscopic data and data based on chemical reactions are not quoted to prove the structure of the final products. It was shown later[83] that the compound obtained under these conditions does not react with maleic anhydride and that there are no absorption bands of the diene chromophore in its UV spectrum (in methanol). It was found that the position of the absorption maximum and its intensity (λ_{max} = 238 nm, ε = 2800) are identical with those calculated for the pentachlorocyclopentene structure. On the other hand, the IR spectrum of this compound contains one narrow absorption band at 1620 cm^{-1}, which is characteristic of the ClC=CCl fragment instead of the two bands which are usual for structures of type (XXXV). The structure of the compound obtained was finally established by analysing its ^1H NMR spectrum using nuclear double resonance. The ^1H NMR spectrum reveals the absence of allylic protons and is fully consistent with the structure (XXXVI). Compound (XXXV) is evidently a precursor in the formation of the final product (XXXVI) via the mechanism



(I) (XXXV) (XXXVI)

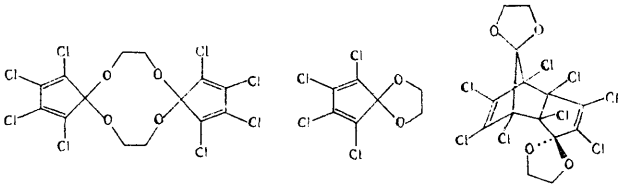
Compound (XXXVI) is formed as a result of the intramolecular [4 + 2]cycloaddition of the intermediate unstable triene (XXXV). The subsequent reaction involving substitution by anions via the S_N1 mechanism in the adduct (XXXV) was not observed under these conditions. However, on refluxing in a methanolic solution of alkali, the product (XXXVI) undergoes a skeletal rearrangement with formation of 4,6-dichloro-3-methoxymethylbenzoic acid (XXXVII), whose structure was determined by spectroscopic and chemical methods: [84]



(XXXVII) (XXXVIII)

The corresponding data confirming the structure (XXXVI) were also obtained almost simultaneously by Jung and Light; [85] in addition, they obtained 15% of the disubstituted product (XXXVIII).

Nucleophilic substitution in HCCPD by various diols has been investigated comprehensively. [86–93] Using ethylene glycolate as the nucleophile, the crystalline compound (m.p. 279 °C), to which the structure (XXXIX) was attributed, had been obtained even earlier: [55]

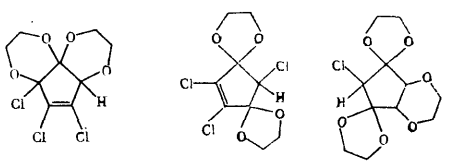


(XXXIX) (XL) (XLI)

It was latter established[87] that, when this reaction is carried out under fairly mild conditions (15 °C) and in the presence of a sixfold excess of ethylene glycol, the formation of low-melting crystals (m.p. 65–66 °C) is observed; the structure of the compound (XL) obtained was determined mainly chemically—by involving it in the diene condensation with various dienophiles. Thus the product was a monomer—a spirodiene.

This reaction was investigated in even greater detail by Chang; [86] three crystalline compounds were then isolated (m.p. 107–108.5°, 79.5–80°, and 64.5–65.5 °C). The substance with m.p. 64.5–65.5 °C, which is 1,2,3,4-tetrachloro-6,9-dioxaspiro[4,4]-nona-1,3-diene (XL), can be obtained in 90% yield from one mole of HCCPD, 2.1 moles of KOH, and 8 moles of ethylene glycol. On heating (2 h, ~100 °C) or on storage in solutions for a fairly long time, compound (XL) dimerises to the product (XLI) (m.p. 279 °C) and not the product (XXXIX). The structure (XLI) was established chemically (this compound is inert to the action of dienophiles) and spectroscopically. The high tendency of the diene (XL) to dimerise, in contrast to the diene (II), has been explained by the steric influence of the ketal group. However, the author did not establish the structures of the other two compounds which he obtained (with m.p. 107–108.5° and 79.5 to 80 °C).

Subsequently, this reaction was investigated[70] at relatively high temperatures (55–60 °C) and mainly five compounds were then obtained: (XL), (XLI), (XLII), (XLIII), and (XLIV).

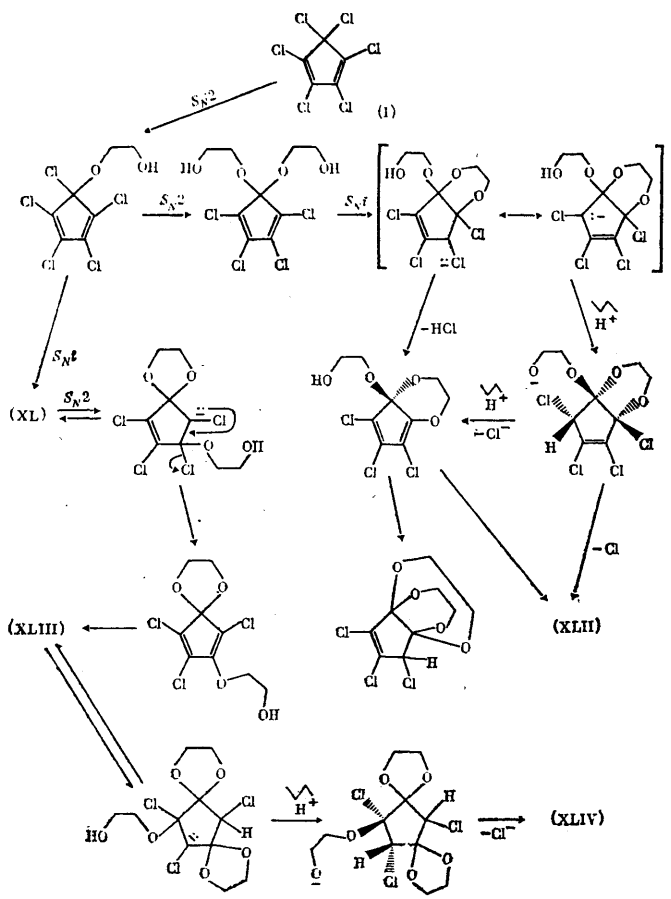


(XLII) (XLIII) (XLIV)

In the presence of an excess of the glycol and alkali and under more severe conditions (50–120 °C) the product (XLII) is formed. (On raising the reaction temperature to

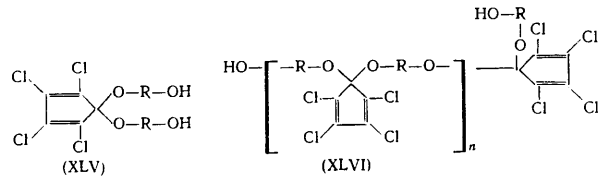
140 °C, the formation of compound (XLIV) is observed.[92] The proposed reaction mechanism[70] is indicated in Scheme 1.

Scheme 1



As can be seen from this scheme, the author attempts to explain the initial attack by the nucleophile from the standpoint of the S_N2 mechanism, but this is impossible, as noted above. On the other hand, the monoalkoxy-intermediate formed should also be converted into the dialkoxy-compound via the S_N1 mechanism and not the S_N2 mechanism.[67,71]

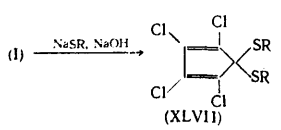
The interaction of HCCPD with polyhydric alcohols containing ≥2 hydroxy-groups, compounds with non-neighbouring carbon atoms, leads to the formation of 1,2,3,4-tetrachloro-5,5-di(hydroxyalkoxy)cyclopentadienes (XLV) and the polyketals (XLVI):[90]



(XLV) (XLVI)

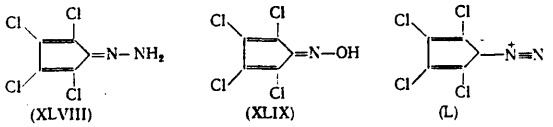
The ratio of the products obtained depends on the stoichiometry of the initial components taken for the reaction.

The reactions between HCCPD and various thiols in alcohol solution, leading to 5,5-thioketals (XLVII), proceed analogously to the reactions of HCCPD with alcohols:[57,94]



(XLVII)

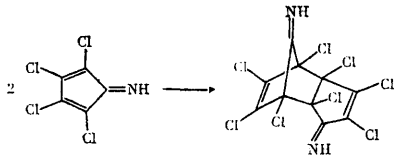
HCCPD reacts actively with hydrazine and hydroxylamine, which results in the formation of tetrachlorocyclopentadienone hydrazone (XLVIII) and oxime (XLIX):[95-98]



(XLVIII) (XLIX) (L)

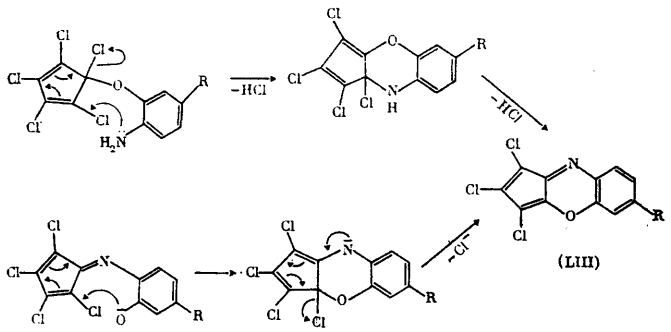
Dehydrogenation of the product (XLVIII) leads to the formation of tetrachlorodiazocyclopentadiene (L) in a high yield. In contrast to 1,2,3,4-tetrachlorocyclopentadienone, the above compounds are stable at room temperature.

It is of interest that the substitution product (LI), obtained by the reaction of HCCPD with ammonia at low temperatures (~−70 °C), is unstable and dimerises at the instant of formation to form the bisimine (LII):[99-100]



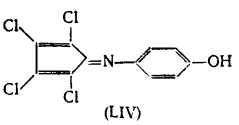
(LI) (LII)

The interaction of HCCPD with *o*-aminphenols in the presence of C_2H_5ONa yields[101] cyclopentabenzoxazines (LIII). The authors quote two alternative mechanisms of formation of the product (LIII):



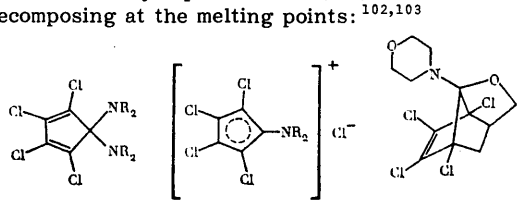
(LIII)

Which of the two nucleophilic centres (NH_2 or OH) is the first to be attacked has been demonstrated by using *p*-aminophenol as the nucleophile, which affords a single product—*p*-hydroxyazafulvene (LIV), which indicates the dominant role of the NH_2 group compared with the hydroxyl in this reaction:



(LIV)

When secondary amines such as morpholine, piperidine, and dimethylamine are used as the nucleophiles, 5,5-disubstituted tetrachlorocyclopentadienes (LV) are formed as a rule, decomposing at the melting points:[102,103]

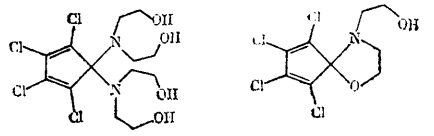


(LV) (LVa) (LVI)

The monosubstituted product (LVa) was not isolated, which the authors explain by its instability when acted upon by bases.

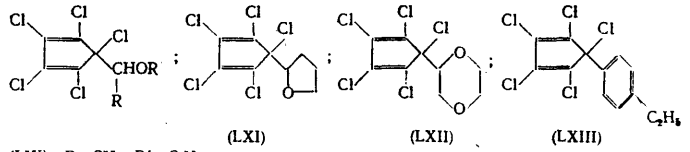
It is curious that treatment of compound (LV) with allyl alcohol for 4 weeks (25 °C) entails the replacement of one morpholino-group by the allylate anion with formation of the oxatricyclononene structure (LVI).

The interaction of diethanolamine with HCCPD led to the spiro-compound (LVIII) and not to the usual substitution product (LVII):[104,105]



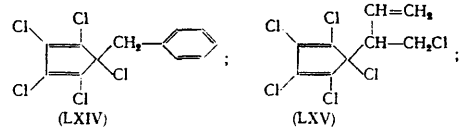
(LVII) (LVIII)

The HCCPD derivatives (LIX)–(LXIX) monosubstituted by functional-groups in the 5-position, synthesised by photo-initiated radical reactions,[106,107] undergo nucleophilic substitution on reaction with two typical nucleophiles: the methoxide anion and morpholine;[45] it was shown that the reaction proceeds in two stages with formation of 5,5-disubstituted products:

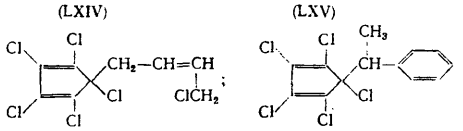


(LXI) (LXII) (LXIII)

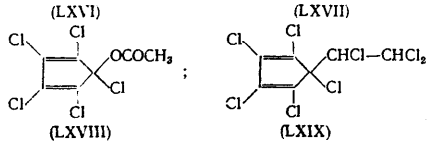
(LIX): R=CH_3, R'=C_2H_5
(LX): R=CH_2Cl, R'=C_4H_9



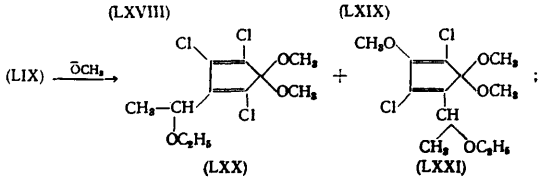
(LXIV) (LXV)



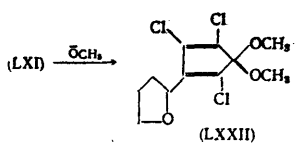
(LXVI) (LXVII)



(LXVIII) (LXIX)



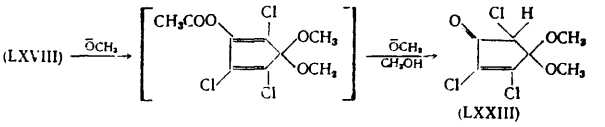
(LXX) (LXXI)



(LXXII)

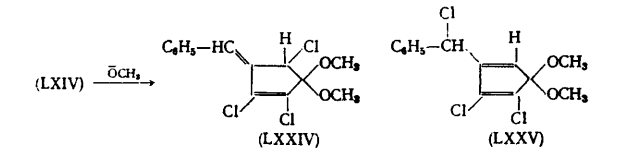
After prolonged heating, the authors were able to isolate the trimethoxy-derivative (LXXI).

The 5-acetoxy-derivative (LXVIII) readily reacts with the methoxide anion, which affords a high yield of the ketone (LXXIII):[45]



(LXXIII)

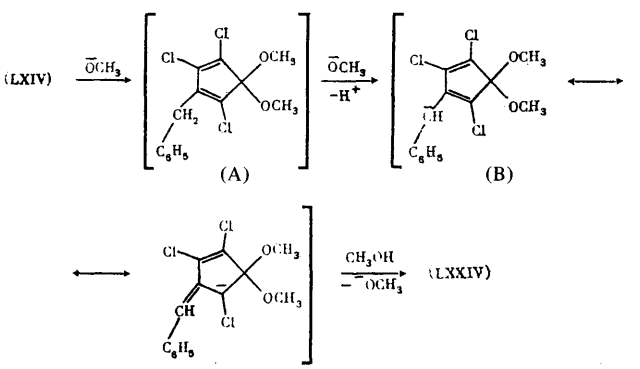
The authors emphasise that the interaction of compounds (LXIV) and (LXVII) with the alkoxide proceeds in a more complex manner and that the rearranged products (LXXIV) and (LXXVII) are then formed in satisfactory yields:



(LXXIV) (LXXV) (LXXVI) (LXXVII)

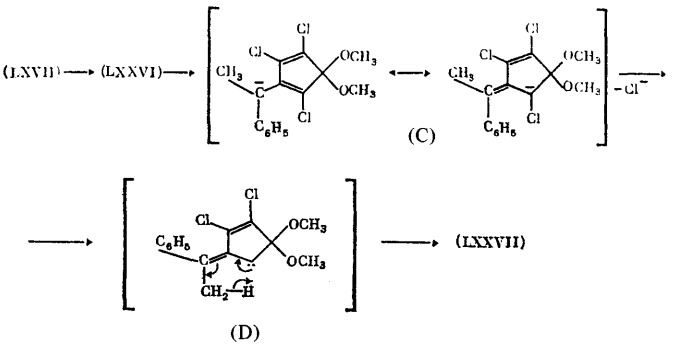
Compound (LXXVI) is fully converted during the reaction into the product (LXXVII). It has been established on the basis of spectroscopic data that the structure (LXXIV) is more probable than the structure (LXXV).

Consequently, the reactions of the benzyl compounds proceed in an unusual manner and involve three stages—methoxylation, dehydrochlorination, and hydrogen transfer from the substituent to the cyclopentadiene ring:



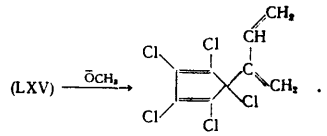
(A) (B) (LXXIV)

Compound (LXXVII) can also be obtained via the above pathway, but the subsequent conversion of the anion (C) into the carbene (D) and the 1,4-sigmatropic shift in the latter lead to the product (LXXVII):



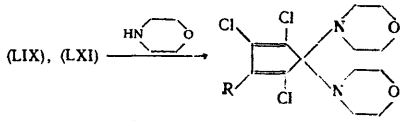
(C) (D)

Treatment of compound (LXV) with an equivalent amount of the alkoxide results in an almost quantitative formation of the bisdiene (LXXVIII):[45]



(LXXVIII)

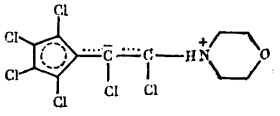
Compounds (LIX) and (LXI) react readily with morpholine, forming the 5,5-disubstituted products (LXXIX) and (LXXX):



(LXXIX), (LXXX)

(LXXIX): R=CH(CH$_3$)OC$_2$H$_5$; (LXXX): R=

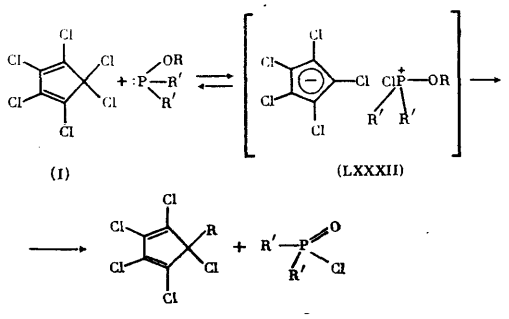
The reaction between the diene (LXIX) and morpholine proceeds differently and results in the formation of a dark-red product having the overall formula $C_{11}H_9Cl_6NO$. The structural formula (LXXXI) was attributed to it from spectroscopic data and physical properties:



(LXXXI)

III. SUBSTITUTION ON TREATMENT WITH TERVALENT PHOSPHORUS AND ORGANOMETALLIC COMPOUNDS

The high tendency of HCCPD to form the stable aromatic pentachlorocyclopentadienyl anion on interaction with tervalent phosphorus and organometallic compounds has led to a new effective way of obtaining halogenocyclopentadienes with functional-group substituents[108–110] and has stimulated the development of the field of halogenophilic reactions.[10] According to the mechanism proposed by Mark,[111] the above reaction is a two-stage process; the allylic chlorine is abstracted by the nucleophile in the first stage with formation of the pentachlorocyclopentadienyl anion (LXXXII), while in the second stage the latter is alkylated with formation of 5-alkylpentachlorocyclopentadiene (LXXXIII):

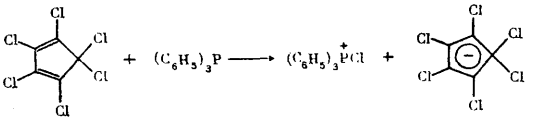


(I) (LXXXII)

(LXXXIII)

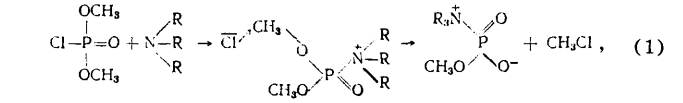
Repeated alkylation of compound (LXXXIII) gives rise to a mixture of three isomers: 5,5-, 1,5-, and 2,5-dialkyltetrachlorocyclopentadienes. Alkylation of HCCPD via the above scheme does not proceed in accordance with the S_N2 mechanism, in contrast to the Arbuzov rearrangement, which has been confirmed by the reactions of sterically hindered phosphites (t-butyl dimethyl phosphite, t-butyl diethyl phosphite) with HCCPD, which lead to the formation of 5-monosubstituted pentachlorocyclopentadienes.

The ^{31}P NMR signal of the chlorotriphenylphosphonium cation (LXXXIV) has been detected on interaction of HCCPD with triphenylphosphine (at −80 °C), which indicates the simultaneous formation of the anion (LXXXII):[112]

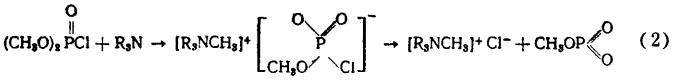


(LXXXIV) (LXXXII)

The use of trimethyl phosphite as the nucleophile led to charring of the reaction mixture as a consequence of the formation of the very reactive intermediate $(CH_3O)_2POCl$ during the reaction. In order to eliminate this difficulty, the equivalent amount of a tertiary amine, which decomposes the undesired product $(CH_3O)_2POCl$ via the mechanisms (1) or (2),[113] was added to the reaction mixture:



(1)

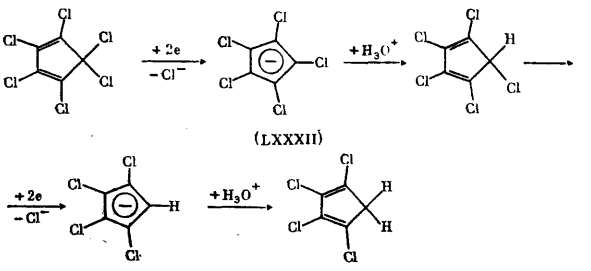


(2)

If the phosphorus atom is the centre of nucleophilic attack, then the reaction proceeds via the mechanism (1).

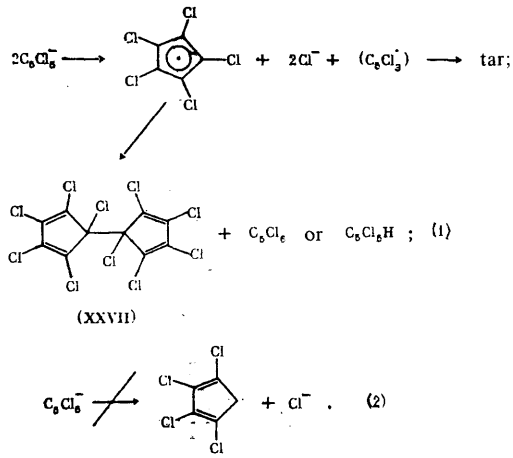
Tri-t-butyl phosphite exhibits a high reactivity in its reaction with HCCPD.[110] The high reactivity of this nucleophile can be accounted for by the high inductive effect of the t-butyl group compared with the normal alkyl groups and also by its large bulk, which increases the O–P–O angle and results in the approach of the hybridisation of the valence electrons of phosphorus to the sp^3 type. This facilitates the transition to the tetracoordinate state.

The formation of the anion (LXXXII) has also been demonstrated by the electrochemical reduction of HCCPD at a dropping mercury electrode in unbuffered and acid aqueous ethanol solutions:[114,115]



(LXXXII)

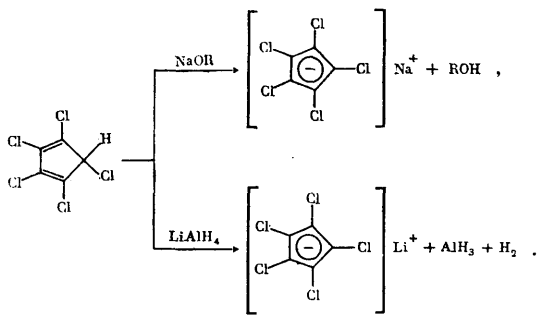
It is noteworthy that the basicity[114] and nucleophilicity[116–118] of the anion (LXXXII) are low, but the anion is rapidly oxidised with formation of the pentachlorocyclopentadienyl radical, owing to the overlap of the occupied π orbitals of the cyclopentadiene ring with the $3p_y$ orbitals of chlorine and this destabilises the π orbitals:



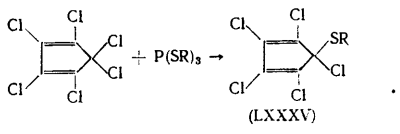
(XXVII)

The isolation of bispentachlorocyclopentadienyl (XXVII) serves as confirmation of the proposed mechanism (1).[116]

The anion (LXXXII) is also readily generated from pentachlorocyclopentadiene by reaction with strong bases:[65,116,118]

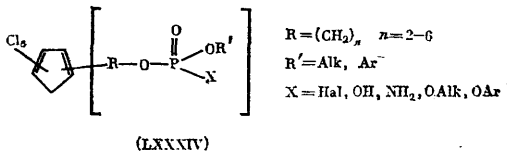


In contrast to the reaction of trialkyl phosphites with HCCPD, the interaction of the latter with trialkyl phosphorothioites leads to the formation of 1,2,3,4,5-pentachlorocyclopentadienyl sulphide (LXXXV), which exhibits a high biological activity:[119,120]



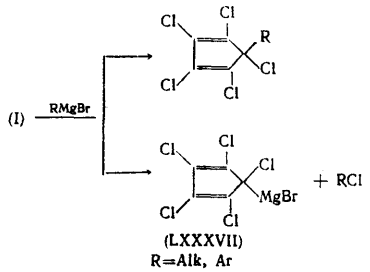
(LXXXV)

In contrast to acyclic phosphites, cyclic phosphites having the general formula OROPOR′, give rise on reaction with HCCPD, to pentachlorocyclopentadienyl phosphates (LXXXVI)[121,122] possessing insecticidal and herbicidal activities:



(LXXXIV)

HCCPD interacts vigorously with Grignard reagents, which results in the formation of monosubstituted products and other secondary compounds:[123,124]



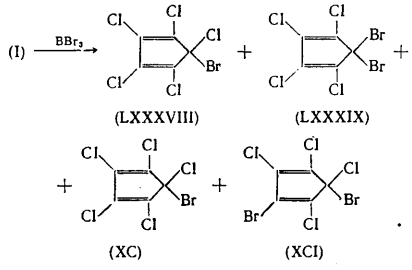
(LXXXVII)
R=Alk, Ar

The authors were unable to obtain a Grignard reagent from HCCPD by the direct interaction of the latter with magnesium owing to the marked charring of the reaction mixture. It was therefore necessary to obtain initially the Grignard reagent of a halogenohydrocarbon and, by the reaction of the latter with HCCPD, to synthesise the desired product (LXXXVII). It was established that one chlorine atom is substituted by MgBr in this reaction, since only 1,2,3,4,5-pentachlorocyclopentadiene and a small amount of its dimer are formed on dilution of the reaction mixture with water. In addition two further compounds were isolated from the reaction mixture—bispentachlorocyclopentadienyl and a hydrocarbon. The interaction of HCCPD with RMgBr and subsequent mixing with solutions of halogenohydrocarbons in ether lead to 5,5-disubstituted derivatives of HCCPD.[123]

The chlorophilic reaction strikingly manifests the extensive synthetic possibilities for the preparation of new HCCPD derivatives with functional-group substituents in the synthesis of mixed polyhalogenocyclopentadienes.[125–132]

During recent years, much attention has been devoted to the synthesis of polyhalogenocyclopentadienes in connection with the vigorous development of ecological chemistry and the chemistry of skeletal compounds with functional-group substituents.[7,125]

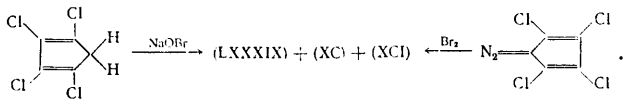
In the temperature range 160–170 °C, HCCPD reacts with PBr_3 to form 5-bromo-1,2,3,4,5-pentachlorocyclopentadiene.[127] In the presence of a catalytic amount of $AlBr_3$, the above reaction with PBr_3 leads to the successive substitution of chlorine atoms by bromine.[128,129] However, the question of the isomerism of the mixed polyhalogenocyclopentadienes obtained was not considered in these investigations and the authors unambiguously attributed structures with bromine atoms at C(5) to the compounds synthesised. ^{13}C NMR has been used to demonstrate the structures.[125] It was established reliably on the basis of the spectroscopic data that the reaction products are 5-bromo-1,2,3,4,5-pentachlorocyclopentadiene (LXXXVIII), 5,5-dibromotetrachlorocyclopentadiene (LXXXIX), 1,5-dibromotetrachlorocyclopentadiene (XC), 2,5-dibromotetrachlorocyclopentadiene (XCI), and a small amount of an extensive bromination product.



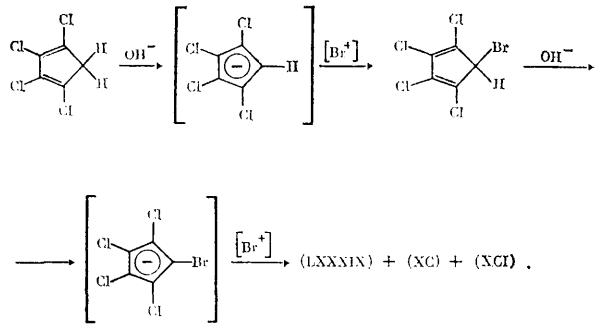
(LXXXVIII) (LXXXIX)

(XC) (XCI)

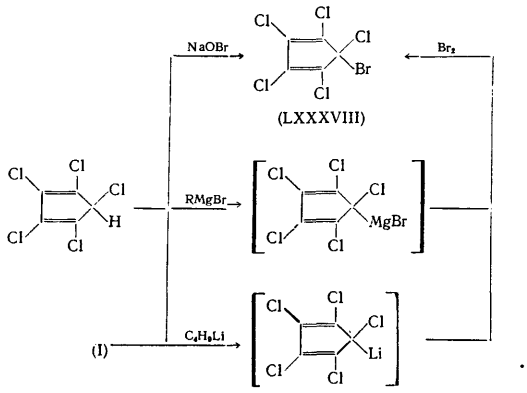
Compounds (LXXXIX), (XC), and (XCI) have been obtained by brominating tetrachlorocyclopentadiene with sodium hypobromite or by the interaction of tetrachlorodiazocyclopentadiene with bromine:[125]



This yields a mixture of three isomers in approximately equal proportions. The simultaneous formation of three dibromide isomers on bromination of tetrachlorocyclopentadiene was explained by the authors[125] with the aid of the following scheme:

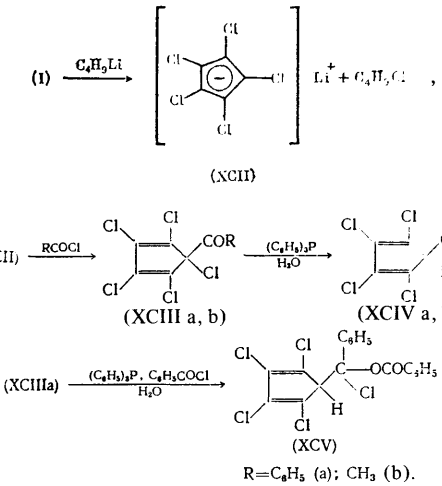


The absence of monobromides with vinyl hydrogen atom from the reaction products indicates the regioselective attack by the electrophilic bromine on the 5-position in the anion (E). However, attack on the anion (F) by the electrophile can also take place non-regioselectively, which in fact results in the formation of three isomers. The monobromide (LXXXVIII) has been obtained by the reaction of pentachlorocyclopentadiene with NaOBr and also by the reaction of pentachlorocyclopentadienylmagnesium bromide or pentachlorocyclopentadienyl-lithium with bromine:[125]



Contrary to the data of Williamson et al.,[130] Zaichikova et al.[125] established, on the basis of chemical reactions and with the aid of ^{13}C NMR, that the bromine atom does not migrate in the cyclopentadiene ring in the monobromide (LXXXVIII) on heating and under the conditions of this diene synthesis.

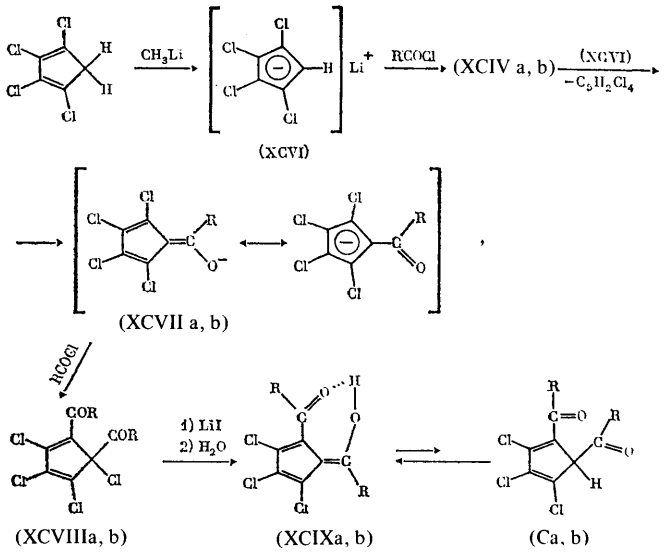
Pentachloro- and tetrachloro-cyclopentadienyl-lithium are widely used in the synthesis of HCCPD derivatives monosubstituted by functional groups.[65,126,133] A new method of synthesis of compound (XLII) has been developed and a number of syntheses based on it have been carried out.[126] In contrast to the known procedures for synthesising compound (XCII) with the aid of lithium amalgam and $LiAlH_4$,[118] it was synthesised from HCCPD and butyl-lithium in pentane at −70 °C and was immediately made to react with strong electrophiles—carboxylic acid chlorides,[126] which results in the formation of unstable 5-acylpentachlorocyclopentadienes (XCIIIa, b):



These ketones (XCIIIa, b) are used in synthesis without additional purification at the instant of their formation, as shown in the scheme.

An unexpected result has been obtained[126] in the reduction of the ketone (XCIIIa) by triphenylphosphine in the presence of an excess of benzoyl chloride. It was established from spectroscopic data that, together with the formation of compound (XCIVa), its enolic form is acylated with the intermediate formation of tetrachlorophenylbenzoyloxyfuvene and the addition to the latter of hydrogen chloride. The structure of compound (XCV) was confirmed by its specific synthesis.

The acetylation of tetrachlorocyclopentadienyl-lithium (XCVI) with acetyl chloride at −50 °C led to the stable crystalline product (XCIXb) whose structure was determined by spectroscopic methods; for example, the signal due to the chelate proton in the ^1H NMR spectrum is in the region of $\delta = 16.10$ p.p.m.



Thus the existing experimental data on nucleophilic substitution in HCCPD demonstrate that this structurally simple compound has interesting chemical properties and reveal the following features of reactions of this type.

Nucleophilic substitution of the chlorine atoms in HCCPD by alkoxides, thiolates, and amines proceeds in two stages: initially the anion attacks the 2-position in HCCPD via the S_N2' mechanism and then the allylic chlorine atom (in the 5-position) is abstracted via the S_N1 mechanism and the final reaction products are 5,5-disubstituted 1,2,3,4-tetrachlorocyclopentadienes.

Substitution by treatment with alkoxides obtained from allyl alcohol and its derivatives proceeds anomalously with formation of 5-monosubstituted products.

Substitution by treatment with tervalent phosphorus and organometallic compounds takes place with formation of the aromatic pentachlorocyclopentadienyl anion, whose alkylation affords 5-alkyl-1,2,3,4,5-pentachlorocyclopentadiene.

However, together with the above findings, there exist also unsolved problems in this field, in particular there are no data concerning the carbanionic (Ad_N type) addition—elimination mechanism, which may compete with the mechanism of the S_N2' type in the reactions of HCCPD with alkoxides (the formation of 1,3,4-trichloro-5,5-difluoro-2-methoxycyclopentadiene on interaction of 1,2,3,4-tetrachloro-5,5,difluorocyclopentadiene, a derivative of a HCCPD homologue, with the methoxide anion can be readily explained with the aid of the Ad_N mechanism[65,71]); the formation of only monosubstituted products in the reaction of HCCPD with certain saturated alcohols is unexpected;[77,78] there have been no quantum-chemical calculations for HCCPD and 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene, with the aid of which it might be possible to predict the regioselectivity of the reactions, etc.

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Institute of Organochlorine
Synthesis, Academy of
Sciences of the Azerbaijan
SSR, Sumgait