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Electrophilic Substitution in Cyclopentadienide Anions

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The considerable new synthetic possibilities, which have arisen as a result of studies on electrophilic substitution reactions in the cyclopentadienide series, are considered in the review. The possible mechanism of these processes is analogous to the mechanism of substitution in the benzene series. Much attention has been devoted to the problem of the direction of electrophilic attack in cyclopentadienide ions containing both electron-donating and electron-accepting substituents. The bibliography includes 63 references.

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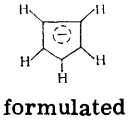
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I. INTRODUCTION

The problem of electrophilic substitution has been most widely studied in the benzene series. However, recently the attention of investigators has been increasingly drawn to problems associated with the study of electrophilic substitution in other aromatic systems, in particular such as the cyclopentadienide ion (CPD ion). The interest in this problem arises mainly from the synthetic requirements which must be met in various substituted cyclopentadienides necessary for the preparation of fulvenes, ylides, sandwich π complexes with transition metals, and many other derivatives. The elucidation of the question of the direction of the electrophilic attack is of particular interest in this problem, since, in contrast to benzene, the cyclopentadienide ion is a non-alternant system.

II. AROMATIC PROPERTIES OF CYCLOPENTADIENIDE IONS

As early as 1901, it was known as a result of Thiele's work[1] that cyclopentadiene exhibits acidic properties†. Thiele found that the potassium salt of cyclopentadiene is fairly stable although very reactive. The high stability of the $C_5H_5^-$ ion was repeatedly confirmed subsequently. In 1928 Goss and Ingold[3] explained the reason for the stability of salts with cyclopentadiene ions by the fact that the six π electrons distributed over the five-membered ring form in this ion an aromatic system resembling that of benzene. On the basis of LCAO-MO calculations, Hückel[4,5] suggested that the cyclopentadienide anion is a stable system, since all four π electrons of the two double bonds and the lone electron pair of the carbon atom remaining after the abstraction of a proton are involved in cyclic conjugation. The negative charge of the cyclopentadienide ion is not localised at an individual carbon atom but is distributed throughout the ion. All the π electrons are located in bonding orbitals, forming a "closed" electron cloud.

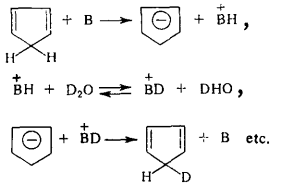


At the same time Hückel formulated the rule of aromaticity.

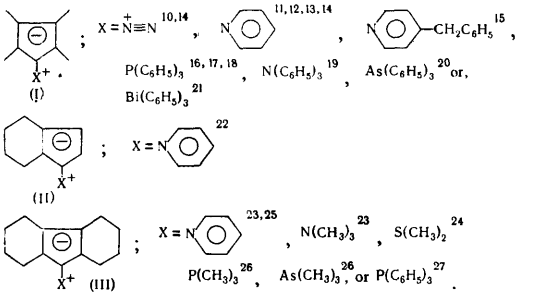
†According to the latest data, $pK = 15$ for cyclopentadiene[2].

Tkachuk and Lee[6] showed experimentally by a tracer atom method (^{14}C) that all five carbon positions in the cyclopentadienide anion are equivalent. Moreover, the equivalence of all five C–C and C–H bonds in the cyclopentadienide ring was demonstrated by X-ray diffraction, electron diffraction, and also spectroscopic methods[7]. The resonance energy for this ion proved to be 48 kcal mole^{-1}.[8]

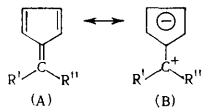
In a study of deuterium exchange in cyclopentadiene, Kursanov and Parnes showed that, in the presence of a base, all six hydrogen atoms are very readily exchanged for deuterium[9]. They also explained this finding by the aromatic properties of the cyclopentadienide ion:



Not only salts with alkali metals and magnesium but also saltlike dipolar compounds containing an organic cation linked by covalent bonds to the cyclopentadienide ion, the so called ylides, are known for cyclopentadienide ions. Usually ylides are unstable compounds but the introduction of the stable aromatic cyclopentadienide ion allows their isolation in a pure form. A wide variety of ylides incorporating cyclopentadienide (type I), indenide (type II), and fluorenide (III) anions linked to the cationic component containing exo- or endo-cyclic atoms of the 'onium-forming elements in Group V (nitrogen, phosphorus, arsenic, antimony and bismuth) and partly Group VI (sulphur) are now known[10-27]:



The study of the dipole moments of certain ylides confirmed their high polarity[28,29]. Fulvenes can be regarded as to some extent of the same type. Their dipole moment is about 1.5 D [30] and the resonance energy is 12 kcal mole^{-1} [31] (i.e. one-third of the resonance energy of benzene). The π-electronic structure of fulvenes can be described by the resonance hybrid of the covalent structure (A) and the polar structure (B):



(A) (B)

where R′ = R″ = H, alkyl, or aryl.

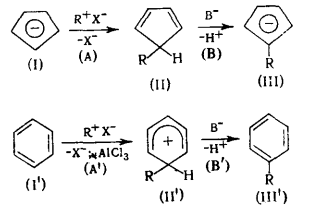
As the electron-donating properties of the substituent at the C_6 carbon atom become more pronounced, the contribution of the polar structure to the resonance hybrid increases. The appreciable contribution of the polar structure is explained, in accordance with Hückel's rule [4,5], by the stability of the cyclic system containing six π electrons.

In contrast to the salts of the cyclopentadienide anion with alkali metals, magnesium, and ammonium cations, the derivatives with transition metal cations lose their ionic properties in most cases. The exceptions will be discussed below. An unusual type of bond, which has been called the π-complex bond, arises under these conditions. The compounds formed, among which ferrocene, nickelocene, and cobaltocene have been most thoroughly investigated, are fairly stable, particularly ferrocene. Dative bonds formed with the *d* electrons of the transition metal make a significant contribution to bond stabilisation in these compounds, in addition to the donor–acceptor bonds.

III. REACTIONS WITH ELECTROPHILIC AGENTS

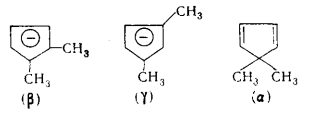
The availability of various cyclopentadienide ions is to some extent limited by the availability of the corresponding cyclopentadienes. The latter may be obtained mainly by two methods: by synthesising the five-membered ring via a cyclisation reaction and by electrophilic substitution in the already existing cyclopentadienide ion. The first method has no direct bearing on the problem under consideration; it is discussed in a useful review by Moritani and Fujiwara [32]. Another method of synthesis, based on the reaction with electrophilic reagents‡, has begun to be developed comparatively recently. It has a number of advantages over the first procedure, since it makes it possible to obtain very complicated derivatives of the cyclopentadienide ion in one or two stages, but, on the other hand, the method is complicated by the formation of side products and involves the necessity to elucidate the direction of electrophilic attack.

The mechanism of electrophilic substitution in the cyclopentadienide ion (stages A and B) is formally similar to the mechanism of electrophilic substitution in the benzene series (stages A′ and B′). [33,34] It is postulated that undissociated cyclopentadienes (II) correspond to the σ complex (II′) in the benzene series:



When various electrophilic agents are employed, the final result in the cyclopentadienide series depends as a rule on whether the substituent introduced is electron-donating or electron-accepting. Since electron-donating substituents increase the electron density of the ring, their introduction results in an increase of the nucleophilicity of the cyclopentadienide ion and, in the presence of sufficient electrophilic agent, it is possible to achieve complete substitution of hydrogen atoms in the initial cyclopentadiene. It is noteworthy that polysubstituted products are obtained even when the initial reactants are employed in 1 : 1 proportions, since some of the cyclopentadienide ions are consumed as a base, as a result of which a certain amount of unsubstituted cyclopentadiene is isolated from the reaction mixture. On the other hand, the introduction of very powerful electron-accepting substituents lowers the nucleophilicity of the cyclopentadienide ion and therefore, under the usual conditions, it is possible as a rule to substitute only two or three hydrogen atoms. Special conditions must be employed to achieve complete substitution.

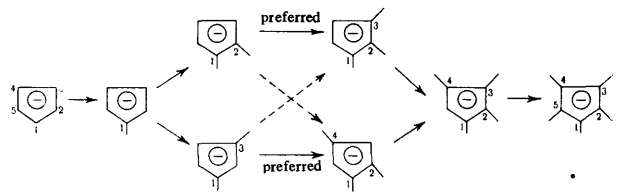
The cyclopentadienide ion can enter into electrophilic substitution reactions even with weak electrophilic agents such as methyl iodide. Thus in 1965 McLean and Haynes [33,34] showed that, depending on the reaction conditions, different mixtures of products are formed. In liquid ammonia in the presence of a deficiency of a base ($NaNH_2$) the reaction can stop at the monomethylation stage. With increase of the methyl iodide: sodium cyclopentadienide ratio, the yield of polymethylated cyclopentadienes rises. A methyl substituent in the ring has a significant influence on the direction of attack. Two isomers (β and γ) are possible for dimethylcyclopentadienide ions. It has been found that the ratio of the disubstituted β- and γ-derivatives is 3.5 : 1:



It is noteworthy that the ratio of the β- and γ-isomers was determined by analysing a mixture of the corresponding dimethylcyclopentadienes by gas–liquid chromatography. The analysis revealed the presence in the mixture also of a small amount (about 1%) of a product with the second methyl group in the α-position. Thus the selectivity series for attack in the methyl cyclopentadienide ion is $\beta > \gamma > \alpha$. It was discovered that the α-position is approximately 5 times less sensitive to attack by the electrophilic agent than even the γ-position. Since the resulting selectivity series for electrophilic attack corresponds to the distribution of electron density in the methyl cyclopentadienide anion [calculated by Hückel's method (Fig. 1)], the authors suggested that the site of electrophilic substitution in the cyclopentadienide ion may be determined by the distribution of electron density in the ring [33].

‡In the present review we are not considering the reactions of the cyclopentadienide ion with electrophilic agents such as the halides of a number of elements (silicon, tin, mercury, etc.), since the description of such data, closely related to the field of metallotropic reactions, would unduly divert the reader's attention from the main topic.

For the same reason, on further methylation the derivatives obtained from 1,2-dimethyl- and 1,2,3-trimethyl-cyclopentadienide ions predominate over the product which might have been expected from 1,3-dimethyl- and 1,2,4-trimethyl-substituted ions:



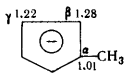
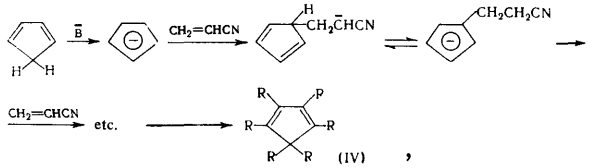


Figure 1. Distribution of electron density in the methylcyclopentadienide ion[33].

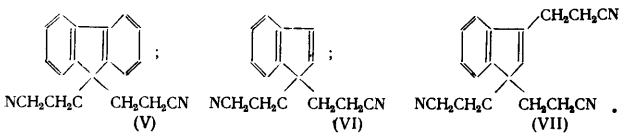
However, Akhrem, Mironov et al.[35], who also made a study of the methylation of sodium cyclopentadienide, note that, when tetramethylcyclopentadienides are employed in this reaction, the *gem*-disubstituted diene is formed in considerable amounts. They believe that in polymethylated cyclopentadienides the site of further alkylation is determined by the operation of factors other than those in the lower homologues.

Another interesting reaction which leads to a substitution product is the cyanoethylation of cyclopentadiene in the presence of a base (benzyltrimethylammonium hydroxide). Unfortunately the details of this reaction have been little investigated, but it is known that, even for equimolar proportions of cyclopentadiene and acrylonitrile, the hexacyanoethylated product (IV) is formed in considerable amounts[36]. The catalytic properties of the base, which are required only to initiate the reaction, are employed:

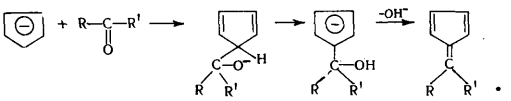


where R = CH_2CH_2CN.

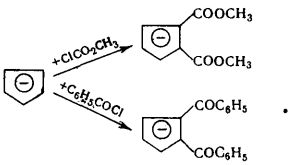
Under the same conditions, fluorene gives the dicyanoethylated product (V) and the reaction of indene with acrylonitrile leads to the dicyanoethylated product (VI) and crystalline tris-(β-cyanoethyl)indene (VII):



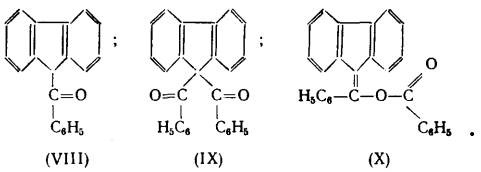
The reaction of aldehydes and ketones with cyclopentadienide ions constitutes the basis of a well known method for the synthesis of fulvenes[37]. The secondary process involving the elimination of the OH ion with formation of the fulvene system completes this reaction:



On the other hand, when electrophilic agents such as methyl chlorocarbonate[38] and benzoyl chloride[39] are employed, the substitution stops at the stage of disubstituted products and in this case, as in the reaction with methyl iodide, the second substituent enters at the β-position relative to the first and the initial cyclopentadienide ion plays the role of a base:

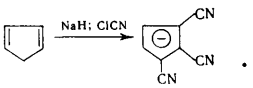


It is noteworthy that lithium fluorenide is also readily benzoylated to a mixture of monobenzoylfluorene (VIII), 9,9-dibenzoylfluorene (IX), and 9,1′-benzoyloxybenzylidenefluorene (X). The relative amounts of the products depend on the nature of the metal and the solvent[40]:

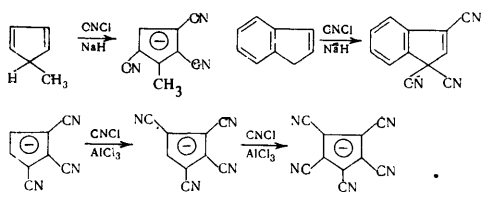


The reaction with cyanogen chloride has been most thoroughly investigated; by this process in the presence of NaH, Webster[41] achieved the substitution of cyano-groups in cyclopentadienides[41].

In contrast to alkyl substituents, the introduction of groups such as CN into the cyclopentadienide ion reduces its nucleophilic activity and therefore the reaction may be stopped at each stage in the presence of a limited amount of cyanogen chloride:



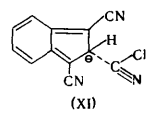
The reaction with cyclopentadiene, methylcyclopentadiene, and indene stops at the stage of the tricyano-product, while tetra- and penta-cyano-derivatives can be obtained from the tricyano-ion only when a Friedel–Crafts catalyst is employed:



The cyano-group is substituted in the tricyanomethylpentadienide anion in the presence of aluminium chloride with formation of tetracyanomethylcyclopentadienide.

In indene the third cyano-group attacks the carbon atom linked to a cyano-group and not a vacant position.

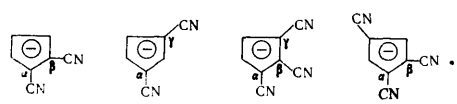
The explanation is that the energy of the transition state (XI) (of the *o*-quinodimethane type) formed on introduction of a cyano-group in a vacant position should be higher:



(XI)

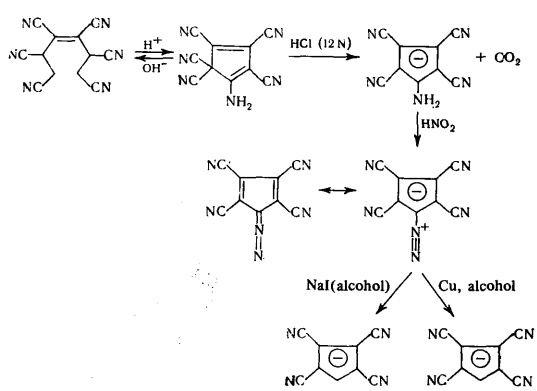
Each cyanocyclopentadienide was isolated and characterised in the form of a potassium or tetraalkylammonium salt. Webster obtained in this way the complete series of cyanocyclopentadienides [41].

The ratio of the $\alpha\beta$-isomer to the $\alpha\gamma$-isomer in dicyano-products is approximately 6 : 1 and in tricyano-products the ratio of the $\alpha\beta\gamma$-isomer to the $\alpha\beta\delta$-isomer is 2 : 1, i.e. the selectivity of the position subjected to electrophilic attack in the substitution of cyano-groups in the cyclopentadienide anion corresponds to the selectivity in its methylation:



It is noteworthy that this method of synthesis of polycyanocyclopentadienides is much simpler than the method based on the cyclisation reaction. As an example, Scheme 1 presents a fairly complex method for the synthesis of the tetracyanocyclopentadienide ion [42,43]:

Scheme 1

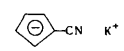
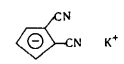
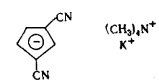
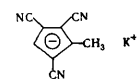
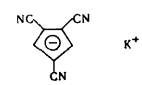
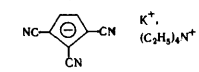
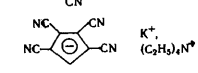
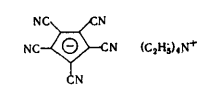


The stability of the resulting cyano-derivatives of the cyclopentadienide ion increases with the number of cyano-groups, as can be seen from the pK_a values for the corresponding conjugate acids (Table 1).

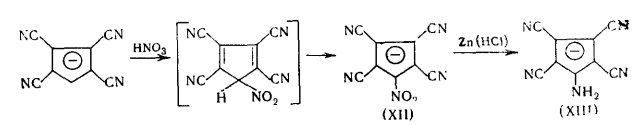
Table 1 shows that tricyanocyclopentadiene is a stronger acid than perchloric acid. The pentacyanocyclopentadienide ion is even more stable. For example, its potassium salt may be heated in air to 400°C without decomposition. The conjugate acid of this anion is very strong: pK_a(in CH_3CN) < -2, for comparison, we have for sulphuric acid pK_a(in CH_3CN) = 7.25. This anion is not protonated even by an acid as strong as perchloric in acetonitrile (spectrophotometric measurements). Probably the pentacyanocyclopentadienide ion has a very strong conjugate acid not only because of the pronounced electron-accepting properties of the five CN groups but also because it has pentagonal symmetry with a uniform delocalisation of the charge in each C–CN group.

It is noteworthy that the pentacyanocyclopentadienide ion and the very stable penta(methoxycarbonyl)cyclopentadienide [44], dicyanodi(ethoxycarbonyl)cyclopentadienide, and tetracyanocyclopentadienide ions [30] do not form ferrocenes on treatment with $FeCl_2$ in consequence of the delocalisation of the negative charge over the electron-accepting substituents. The derivatives obtained proved to be iron(II) salts. The iron(II) tetracyanocyclopentadienide salts are involatile and extremely sensitive to the action of air. These properties indicate an ionic and not a π-complex state of divalent iron.

Table 1. pK_a values for cyanocyclopentadienes in water and acetonitrile [41].

№	Conjugate base	pK_a (in water)	pK_a (in CH_3CN)	pK_a (calc.)
1		15 [2]	—	—
2		9.78	—	—
3		2.52	—	—
4		1.11	10.17 10.17	1.1
5		—	3.40	−5.7
6		—	3.0	−6.1
7		—	1.44 1.99	−7.8 −7.2
8		—	0.0 0.2	−9.1 −8.9
9		—	<−2	<−11
10	$HClO_4$	—	1.83	−7.3 −6.7

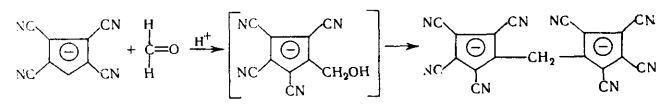
Acid electrophilic agents cannot be employed with unstable cyclopentadienide ions. However, in those cases where the basicity of the cyclopentadienide ion is greatly reduced by the introduction of electron-accepting groups, it is possible to employ also electrophilic agents which are strong acids. Thus concentrated nitric acid nitrates the tetracyanocyclopentadienide ion in 15 min (yield 67%) with formation of the tetracyanonitrocyclopentadienide ion (XII),



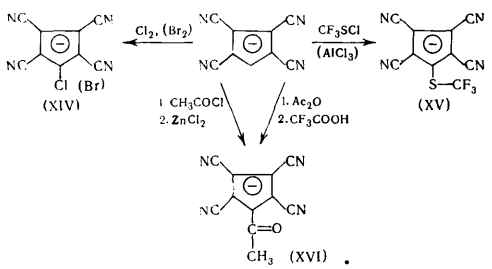
(XII) (XIII)

which could be reduced with zinc dust in hydrochloric acid to the already known [42] aminotetracyanocyclopentadienide

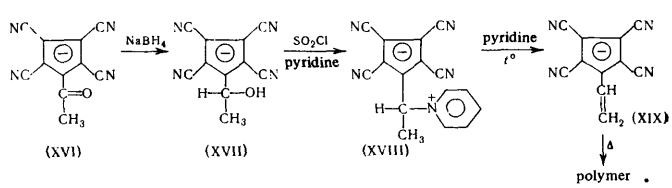
ion (XIII). The reactions of tetracyanocyclopentadienide with formaldehyde and acetaldehyde also take place in an acid medium [45]:



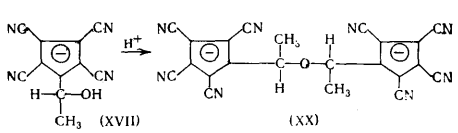
Friedrich [46] and Webster [45], who investigated electrophilic substitution in the tetracyanocyclopentadienide ion, believe that the reactivity of the latter resembles very closely that of anisole. Indeed, like anisole, the tetracyanocyclopentadienide ion reacts readily with halides, but for the reaction with trifluoromethanesulphenyl chloride, acetyl chloride, and acetic anhydride, catalysts of the Friedel-Crafts type or strong acids are required:



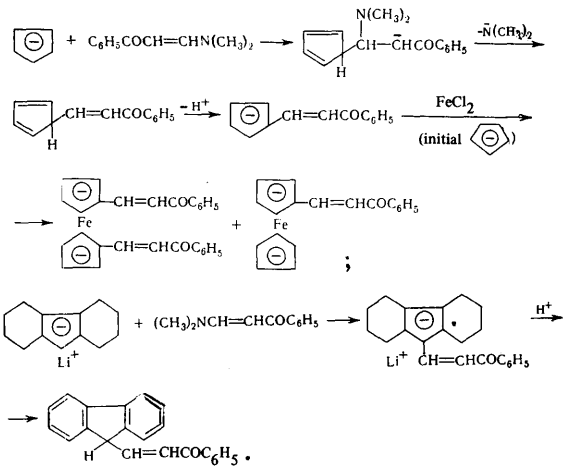
It is noteworthy that the high stability of polycyanocyclopentadienides made it possible to obtain a wide variety of their derivatives. Thus acetyltetracyanocyclopentadienide (XVI) was obtained for the synthesis of tetracyanovinylcyclopentadienide (XIX) according to the following mechanism:



Tetracyanovinylcyclopentadienide (XIX), which was isolated as the tetraethylammonium salt, readily polymerises at 135°C, giving a polymer soluble in acetonitrile. A suspension of the polymer in water may be used as an ion-exchange resin. It is interesting to note that the alcohol (XVII) formed as an intermediate in this synthesis reacts rapidly even with dilute acids to form the dianion of the ether (XX), probably via tetracyanomethylfulvene:

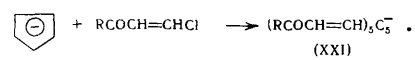


In contrast to polycyano-derivatives, monocyanocyclopentadienide ions, for example 9-cyanofluorene, readily react also with weak electrophilic agents such as alkyl halides [47-49]. By varying the activity of various electrophilic ketovinylating agents, Nesmeyanov and coworkers [50,51] achieved the mono- and poly-ketovinylation of cyclopentadienide ions. The reaction of sodium cyclopentadienide with β-dimethylaminovinyl phenyl ketone gave a monoketovinylated cyclopentadienide, which was identified in the form of ferrocene derivatives:



In this reaction lithium fluorenide gives, after treatment with acid, a high yield of monoketovinylated fluorene.

When a more active electrophilic agent (a β-chlorovinyl ketone) is employed, the reaction does not stop at the monoketovinylation stage but gives rise to coloured polyketovinylated ions, which according to spectroscopic data are most likely to have structure (XXI):



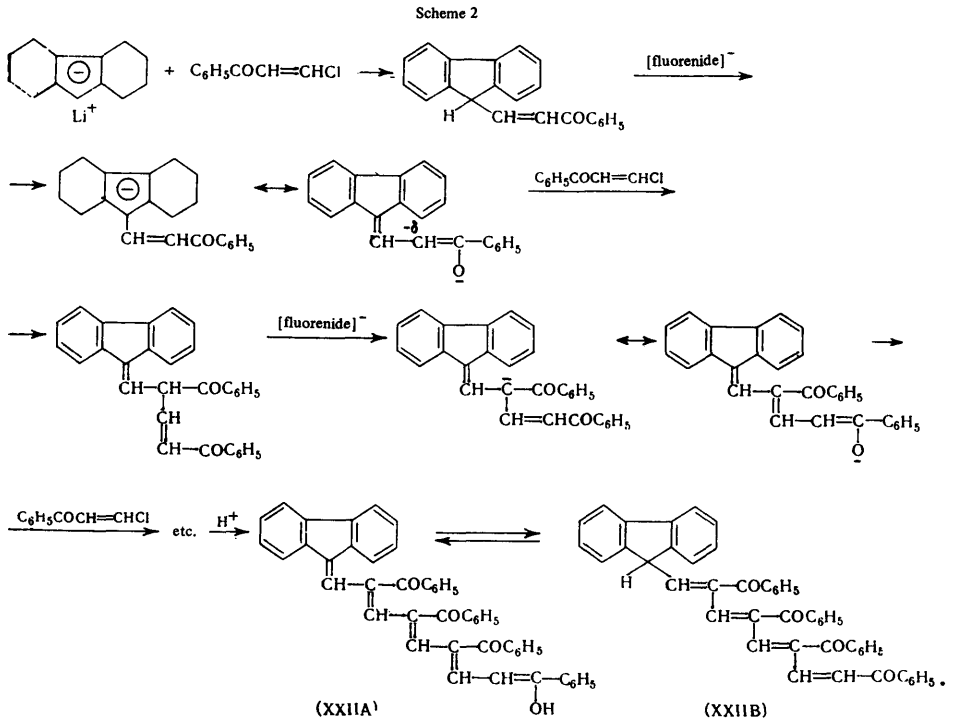
The introduction of five ketovinyl groups into the cyclopentadienide ion can be explained if one remembers that these groups have comparatively weak electron-accepting properties§ and are associated with a considerable steric effect, which lowers the delocalisation of the negative charge owing to the mutual displacement of these groups from the ring conjugation plane. The corresponding conjugate acids of these ions are comparable in strength to carbonic acid (for R = CH_3, pK_a = 7.2 in 50% aqueous alcohol and pK_a = 6.2 in water, while for R = C_6H_5, pK_a = 7.7 in 80% alcohol). However, such delocalisation of the negative charge and possibly also the appreciable steric hindrance proved to be the reason for the inability of the pentaketovinylated ions to form the corresponding ferrocenes on treatment of their sodium salts with iron(II) chloride.

The highly specific behaviour of these ketovinylating agents (RCOCH = CHCl) was noted in relation to lithium fluorenide, which has only one unsubstituted position in the five-membered ring. Whereas with a β-aminovinyl ketone (see above) a monoketovinylated ion was obtained, the reaction with β-chlorovinyl phenyl ketone yielded, after hydrolysis, an orange-red cryptocrystalline tetraketovinylated product, the structure of which has one of two tautomeric forms (XXII, A) or (XXII, B) (Scheme 2) according to molecular weight determinations (mass-spectrometric analysis), spectroscopic characteristics, and chemical reaction data:

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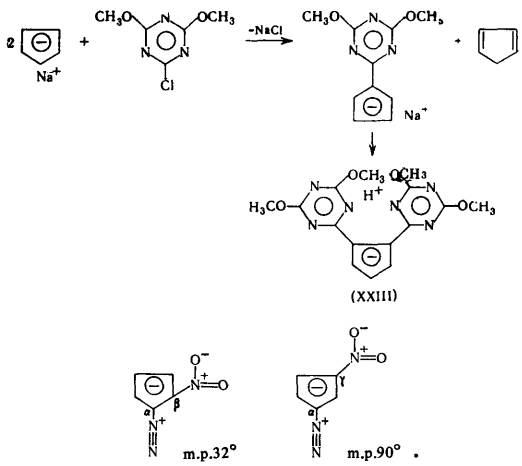
§If one remembers that the transmission coefficient of the *trans*-vinylene group [52] is about 0.5, the electron-accepting properties of the ketovinyl group are seen to be approximately twice as weak as those of the corresponding acyl groups.

Scheme 2

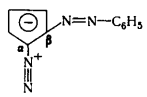


The reaction with 2-chloro-4,6-dimethoxy-*s*-trazine, which leads to the disubstituted product (XXIII),[53] should also be included among the electrophilic substitution reactions of cyclopentadienide ions.

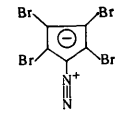
Ylides too are capable of electrophilic substitution reactions. Thus diazocyclopentadiene undergoes electrophilic substitution without the disruption of the ylide π-electron system, attack at the β-position predominating over attack at the γ-position[54]. In the nitration of diazocyclopentadiene the β-substituted product predominates over the γ-substituted product by a factor of 2:



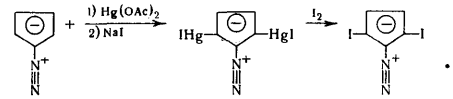
The reaction of phenyldiazonium tetrafluoroborate with diazocyclopentadiene also gives a product substituted in the β-position:



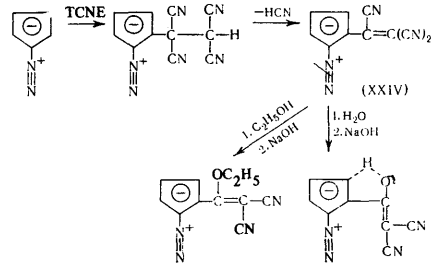
whereas bromination gives tetrabromodiazocyclopentadiene:



On mercuration, diazocyclopentadiene is converted into a very unstable 2,5-bis(iodomercuri)-derivative, which is readily converted into 2,5-di-iododiazocyclopentadiene:

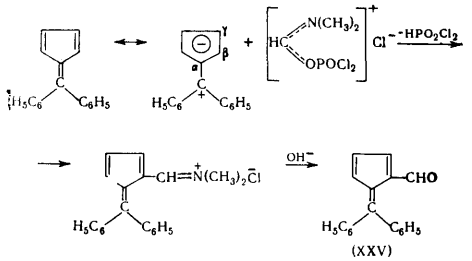


On reaction with tetracyanoethylene, diazocyclopentadiene forms an unstable acid, which easily loses HCN with formation of compound (XXIV), but the Diels–Alder reaction does not occur. Compound (XXIV) undergoes hydrolysis and ethanolysis typical for tricyanoethylenes[55,56]:



Electrophilic substitution in fulvenes has been little investigated. However, fulvenes are capable of electrophilic substitution like other non-benzenoid aromatic systems. Thus 6,6-diphenylfulvene (XXV) is readily formylated with a high yield on treatment with the

Vilsmeier complex[57]. In all the cases investigated, it was found that electrophilic attack on compound (XXVI) takes place at the β-carbon atom[58]:

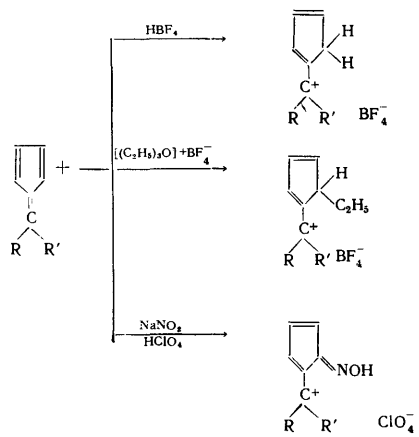


(XXV)

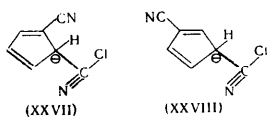
6,6-Diphenyl and 6,6-dimethyl-fulvenes are protonated, alkylated, and nitrosated at −80°C giving the corresponding cyclopentadienes, which are stable only at −80°C[59] (see below).

---oOo---

Thus electrophilic attack on all the cyclopentadienide ions investigated, containing both electron-accepting and electron-donating groups, is directed to the β-position. However, whereas in the presence of electron-donating groups substitution in the β-position could be explained on the basis of the distribution of electron density in the ring, with electron-accepting substituents an enhanced reactivity in the γ-position might have been expected.

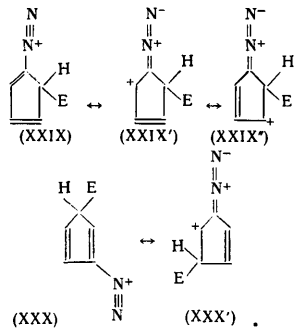


Therefore Webster[41] explains the higher content of the isomer with the CN group in the β-position in the reaction mixture obtained on substituting cyano-groups in the cyclopentadiene ion by the formation of a more stable transition state (XXVII), in consequence of the conjugation of the CN group with a diene system, compared with the transition state (XXVIII) in γ-substitution (a cross-conjugated system):



(XXVII) (XXVIII)

Cram and Partos[54], who studied electrophilic substitution in diazocyclopentadiene, explain their results similarly. They believe that the transition state in β-substitution is more stable, since the cation (XXIX) formed can be represented by three main contributions to the resonance hybrid [(XXIX) ⟷ (XXIX′)↕(XXIX″)], whereas the cross-conjugated cation (XXX) corresponding to γ-substitution has only two contributions [(XXX) and (XXX′)]:



(XXIX) (XXIX′) (XXIX″)

(XXX) (XXX′)

Table 2. Localisation energies (−β).

Model	2-Position	3-Position
	1.149	1.356
	1.685	1.734

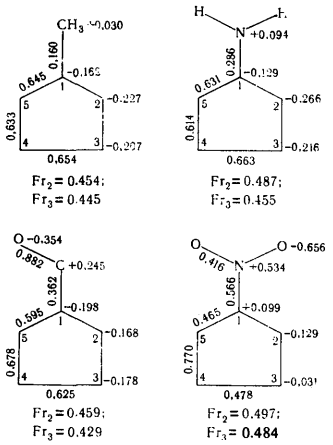


Figure 2. Molecular diagrams for cyclopentadienide ions containing electron-donating and electron-accepting substituents. The numerals against the carbon atoms denote the π-electronic charge and the numerals above the bonds denote the bond order. Fr = free valence index.

A general explanation covering cyclopentadienide ions with electron-donating and electron-accepting substituents is provided by the molecular orbital method. Indeed these results agree with the calculated (by the molecular orbital method) localisation energies (they usually vary in parallel with the free valence index) for monosubstituted cyclopentadienide radicals (Table 2).[60]

The authors note that the results of the calculation should be essentially proved also for the cyclopentadienide ions.

Calculations of the molecular diagrams presented below (Fig. 2) show that the higher reactivity of the β-position in relation to electrophilic substitution in derivatives with electron-donating substituents (CH_3 and NH_2 groups) is indicated both by the π-electronic charge and the free valence index. In the case of electron-accepting substituents, the free valence index again shows the β-position to be more reactive. Calculation of the π-electron density in terms of the Hückel approximation gives a less clear picture. In the presence of an electron acceptor as powerful as the NO_2 group, the β-position is found to have the highest π-electron density. The apparently unusual distribution of electron density under the influence of an electron-accepting substituent is associated with the non-alternant structure of the cyclopentadienyl ring. In the case of the carbonyl group the β-position has a somewhat lower electron density but only slightly so. Evidently calculation taking into account interelectronic interactions would suggest the opposite behaviour also in the presence of the carbonyl group (see the analogous case discussed by Bochvar et al.[61]). Thus the higher reactivity of the β-position regardless of the type of substituent is fully consistent with the π-electron reactivity indices of the substituted non-alternant cyclopentadienyl ring.

It is noteworthy that the electrophilic attack on the β-position observed in the case of fulvenes is also consistent with the calculated distribution of electron density and localisation energy[62,63].

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