U.D.C. 547.834.31

ADVANCES IN THE CHEMISTRY OF THE TROPYLIUM ION

G. D. Kolomnikova and Z. N. Parnes

CONTENTS

I. Introduction 735

II. Acidity of substituted tropylium ions 735

III. Reactions with transfer of electrons to the tropylium ion 738

IV. Sandwich compounds of the tropylium ion 742

V. Formation of the tropylium ion and its properties 745

I. INTRODUCTION

The tropylium cation, predicted in 1931 by Hückel[1] and obtained in 1954 by Doering and Knox[2], constitutes a non-benzenoid aromatic system. According to Vol'pin's definition, "those unsaturated cyclic compounds are aromatic in which all the atoms in the ring are involved in the formation of a single conjugated system, the π-electrons of the system forming a closed† electron shell"[3].

In fact, the seven-membered tropylium ring has a sextet of π-electrons, like benzene and the cyclopentadienyl anion, i.e. it obeys Hückel's rule. Calculation shows that the six π-electrons of the tropylium ion are distributed among the bonding molecular orbitals and form a closed electron shell; the removal and addition of electrons increase the total energy of the system, lowering its stability. The planar structure of the ions follows from X-ray diffraction data[4]. The identity of all seven carbon atoms in the tropylium ion and hence the equality of all the carbon–carbon bonds in the ring have been demonstrated by the radioactive tracer method[5]. The high degree of symmetry of the tropylium cation is also reflected in a small number of infrared and Raman absorption bands[2,6].

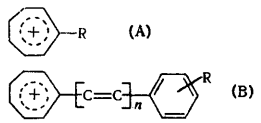
From the chemical point of view, the aromaticity of the tropylium ion is shown in the ease of its formation. The tropylium ion forms under the action of oxidising agents, including hydride ion acceptors (see p. 746), on cycloheptatriene, in the degradation of cycloheptatriene derivatives under the action of electrophilic agents (see p. 747), and when isomeric C_7H_8 hydrocarbons are subjected to electron impact in a mass spectrometer (see p. 748).

The tropylium cation is extremely stable to the action of electrophilic agents[7], exhibiting at the same time high reactivity towards nucleophilic agents[3,8]. Many examples confirming the high electrophilicity of the tropylium cation are known at the present time. Thus the cation combines with many nucleophilic agents[9]. In particular, the tropylium ion is used for the investigation of hydride migration reactions as a hydride ion acceptor[10]. It readily alkylates double bonds activated by electron donor substituents and compounds with "labile" hydrogen (see p. 749). Reactions involving nucleophilic substitution of one group by another are characteristic of the tropylium system[8,11,12]. These properties of the tropylium ion make it a splendid model for the investigation of the properties of carbonium ions, in most cases unstable, which are formed in many chemical reactions as transient intermediates.

The advances achieved in the chemistry of the tropylium ion up to 1960 have been described in Vol'pin's review[3]. In recent years the number of papers on the chemistry of the tropylium ion has increased greatly and in many of them new problems have been posed. We thought it timely to describe in detail problems which were not discussed or discussed superficially in Vol'pin's review. Chapters II, III, and IV of our review deal with these new problems in the chemistry of the tropylium ion. In Chapter V we attempted to describe briefly the papers in which the problems posed in the previous reviews have been developed and new evidence concerning them has been obtained.

II. ACIDITY OF SUBSTITUTED TROPYLIUM IONS

The stability of the tropylium ring changes on introduction of a substituent. Let us consider the effect of substituents on the stability of cations of three types:



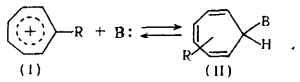
benzotropylium derivatives (C)

The pK_a values for the acid–base equilibrium

$$R^+ + 2H_2O \rightleftarrows ROH + H_3O^+$$

can serve as quantitative characteristics of the stability of carbonium ions. The higher is the pK_a of the carbonium ion the lower is its acidity and, as a rule, the higher its stability in relation to nucleophilic agents. Table 1 lists the pK_a values for the most stable carbonium ions[2,13,14].

In the study of the effect of the substituent on the acidity of the tropylium cation it is necessary to take into account the energy of the conjugation of the substituent both with the tropylium system (I) and the cycloheptatriene system (II):



(I) (II)

If the difference between the conjugation energies of the unsubstituted and substituted tropylium ion (I) is higher than the difference between the conjugation energies of the

TABLE 1.

Cation	pK_a	Cation	pK_a
Tropylium	+4.75*	Triphenylmethyl	−6.63**
Tri-p-anisylmethyl	+0.82**	Diphenylmethyl	−13.3**
Tri-p-tolylmethyl	−3.56**	Fluorenyl	−14.0**

* Measurements in water.

** Measurements in sulphuric acid.

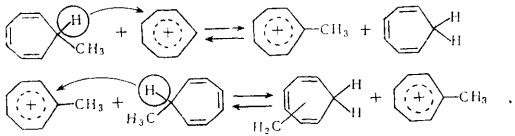
† In the sense given to this term by Hückel.

unsubstituted and substituted cycloheptatriene (II), then, other conditions being equal (change in hybridisation, entropy and solvation effects), electron-donor substituents which delocalise the positive charge of the tropylium ion will reduce its acidity, i.e. its pK_a value will increase. Electron-acceptor substituents should increase the acidity of the tropylium ion. This relation between the acidity and the electron-acceptor or electron-donor properties of substituents has been observed for cations of types (A) and (B), a larger pK_a value indicating in this case a higher stability of the substituted tropylium ion.

If the substituent has a greater effect on the cycloheptatriene system than on the tropylium system, then on introduction of electron-donor substituents delocalising the positive charge of the tropylium ion the acidity of the latter will increase, i.e. the pK_a value will fall. The introduction of electron-acceptor substituents should in this case lead to an increase of the pK_a value. An example of this type of effect of substituents on the acidity of the tropylium ion is the acidity of benzotropylium cations [15-19].

At present there are few data concerning the acidity of substituted tropylium ions of type (A). Johnson et al.[20] showed that the introduction of the electron-acceptor carboxy-group into the tropylium ring lowers the pK_a value from +4.75 for the unsubstituted tropylium ion to +3.3 for the carboxytropylium ion, i.e. reduces the stability of the cation. On the other hand, the introduction of the electron-donor methyl group enhances the stability of the tropylium ion. The acidity constant of the methyltropylium ion has not been measured. However, the stability of tropylium ions can be inferred from the free energy responsible for their reactivity.

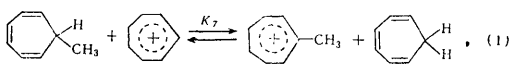
Conrow[21] showed that the free energy of the methyltropylium ion is smaller by 3.7 kcal mole^{-1} than that of the unsubstituted tropylium ion. He investigated the isomerisation of 7-methylcycloheptatriene under the action of the tropylium ion and showed that under these conditions unsubstituted cycloheptatriene forms in addition to the isomeric methylcycloheptatrienes. During a certain period the amount of cycloheptatriene remains constant and no longer changes, while the amount of 7-methylcycloheptatriene continues to decrease. These results enabled Conrow to propose the following reaction mechanism:



The tropylium ion removes a hydride ion from the 7-methylcycloheptatriene molecule with formation of cycloheptatriene and a methyltropylium ion. The latter enters into a further reversible hydride transfer reaction with methylcycloheptatriene.

To confirm this mechanism, Conrow investigated the reduction of the methyltropylium ion with lithium aluminium hydride, sodium borohydride, and calcium hydride. It was found that the relative amounts of methylcycloheptatrienes obtained in this case, where hydride transfer undoubtedly takes place, are approximately the same as in the isomerisation of 7-methylcycloheptatriene.

Knowing the relative amounts of the isomeric methylcycloheptatrienes in the reaction of the methyltropylium ion with lithium aluminium hydride, and also having determined chromatographically the yield of each isomeric methylcycloheptatriene in the isomerisation reaction, Conrow calculated the free energy of the equilibrium reaction (1),

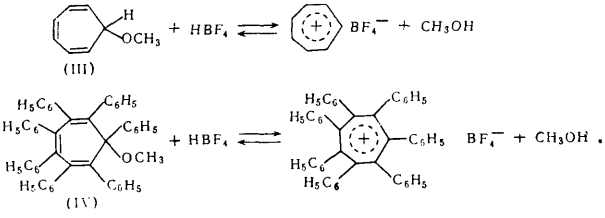


i.e. $\Delta F_7 = -3.72$ kcal mole^{-1}.

Conrow suggested that the resonance energies of 7-methylcycloheptatriene and cycloheptatriene are equal (to within not more than 0.3 kcal mole^{-1}) and their solvation conditions are the same, so that the free energy of reaction (1) can be attributed only to the difference between the free energies of the tropylium and methyltropylium ions. This difference is 3.7 kcal mole^{-1}. Having obtained this quantity, Conrow calculated the free energy differences between the isomeric methylcycloheptatrienes. It follows from his calculations that the methyl group stabilises the tropylium ion much more (by 3.7 kcal mole^{-1}) than the cycloheptatriene molecule (by 1.61 kcal mole^{-1} for 7-methylcycloheptatriene) and therefore the tropylium ion is a better hydride ion acceptor (and in general an acceptor of nucleophilic species) than the methyltropylium ion and 7-methylcycloheptatriene is a better hydride ion donor than cycloheptatriene.

Thus Conrow demonstrated, for the methyl group as an example, that a substituent in cations of type (A) has a greater effect on the tropylium ring than on the cycloheptatriene system. The phenyl substituent is known to have an electron-donor effect in some cases[22] and an electron-acceptor effect in others[23]. It has been found that the phenyl group behaves as a weak electron-acceptor substituent in relation to the tropylium ion. The acidity constant pK_S of the phenyltropylium ion[24], measured by Jutz‡, is +3.87. The acidity constant of the tropylium ion in the 1 : 1 acetonitrile–water mixture is $pK_S = 4.01$. Thus the phenyl group destabilises the tropylium ion. Jutz explains this finding by the fact, shown by calculations, that the benzene and tropylium rings are inclined at an angle 45–50°. Such disposition of the rings results in a decrease of the conjugation between the benzene and tropylium systems and the negative inductive effect of the phenyl substituent may be increased thereby.

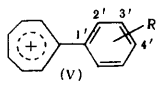
The introduction of seven phenyl substituents destabilises the tropylium ion even more. Due to the very low solubility of heptaphenyltropylium salts, the pK_a value for this ion could not be measured. However, Battiste[25] showed that in a 1 : 1 methanol–acetonitrile mixture methoxycycloheptatriene (III) is fully ionised, with formation of the tropylium ion, under the action of 0.01 N fluoroboric acid, while heptaphenylmethoxycycloheptatriene (IV) is ionised to an extent less than 10% under the action of 1 N acid in the same solution:



‡ Here and henceforth pK_S denotes pK values for carbonium ions measured in a 1 : 1 acetonitrile–water mixture, as was done by Jutz.

Consequently the pK_a value for the heptaphenyltropylium ion is lower by 3 pK units for the tropylium ion, i.e. the heptaphenyltropylium ion is less stable than the tropylium ion in a 1 : 1 methanol–acetonitrile solution by a factor of at least one thousand. It follows from what has been said above that very little is known about the effect of substituents in tropylium ions of type (A) and the quantitative data which have been obtained can be compared only qualitatively.

The effect of substituents bound to the tropylium ring via a benzene ring and a conjugated system of double bonds [cations of type (B)] has been investigated in fair detail. Jutz[24,26] measured the pK_S values for phenyltropylium (V) salts with substituents in the benzene ring.



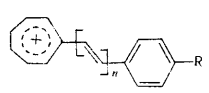
(V)

It was found that these pK_S values are linearly related to Jaffe's σ constants for the substituents [apart from $N(CH_3)_2$], i.e. Hammett's equation holds (see Fig. 1):

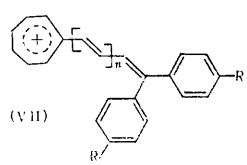
$$pK_s = pK_0 - \sigma\rho;\ \rho = +2.4\ .$$

The positive value of ρ shows that electron-donor substituents reduce the acidity of the phenyltropylium ion, i.e. increase its pK_S value, while electron-acceptor substituents increase its acidity, i.e. lower the pK_S value.

Bearing in mind the disposition of the benzene and tropylium rings at an angle of 45–50°, it may be supposed that in this case the effect of substituents is transmitted as follows: the effect of the substituent R is transmitted by conjugation and inductive mechanisms to position 1′ of the benzene ring in compound (V) and from position 1′ it is further transmitted by an inductive mechanism to the tropylium ring. The introduction of 1, 2, 3, and 4 double bonds between the tropylium and benzene rings in the phenyltropylium ion reduces the acidity of the latter. The pK_S values obtained by Jutz[27,28] for compounds (VI) and (VII) are given below:



(VI)

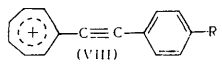


(VII)

for (VI)	R=H	for (VII)	R=H
n	pK_s	n	pK_s
0	3.87	0	4.23
1	4.13	1	4.35
2	4.70	2	4.56

The stabilising effect of conjugated double bonds can be understood if account is taken of their capacity to distribute the positive charge over a large number of centres.

In contrast to the double bond, a triple bond between the tropylium and benzene rings in the phenyltropylium ion greatly increases the acidity of the latter, i.e. decreases the pK_S value: pK_S = +2.40 for the phenylethynyltropylium ion (VIII, R = H)[27], while for the phenyltropylium ion pK_S = +3.87



(VIII)

Consequently the triple bond acts as a powerful electron-acceptor group. It has a similar effect on the ionisation

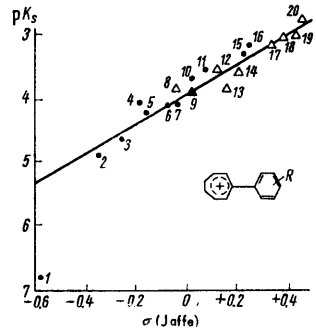
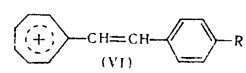


Fig. 1. Variation of the acidity constants pK_S of phenyltropylium cations with Jaffe's σ constants; the substituent R:
1) p-$N(CH_3)_2$; 2) p-OH; 3) p-OCH_3; 4) p-$C(CH_3)_3$; 5) p-CH_3; 6) p-$NHCOC_6H_5$; 7) p-SCH_3; 8) m-CH_3; 9) H; 10) p-C_6H_5; 11) p-F; 12) m-OCH_3; 13) β-naphthyl instead of C_6H_4R; 14) m-C_6H_5; 15) p-Cl; 16) p-Br; 17) m-F; 18) m-Cl; 19) m-Br; 20) m-CF_3.

of acids, for example. Thus phenylpropiolic acid is one hundred times stronger than benzoic acid, while cinnamic acid is somewhat weaker than benzoic acid (see Table 2).

The substituents R in the series of compounds (VI), (VII), and (VIII) have qualitatively the same effect on the stability of the tropylium ion as in the series of compounds (V), namely electron-donor substituents decrease the acidity of the cation, while electron-acceptor substituents increase it. The following pK_S values may be quoted as an example for the styryltropylium series (VI, n = 1):



(VI)

R	H	CH_3	OCH_3	Br	C_6H_5
pK_s	4.13	4.25	4.89	3.82	3.78

However, in contrast to series (V), Hammett's equation does not hold in these cases.

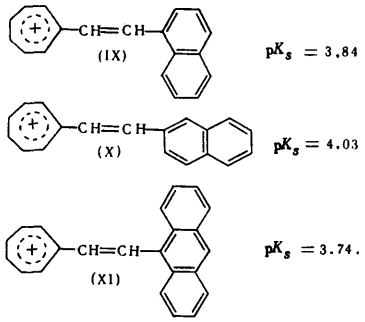
Thus one may conclude that the acidity of tropylium ions of type (B), like that of ions of type (A), increases and decreases respectively in the presence of more powerful electron-acceptor and electron-donor substituents.

The enhanced acidity of (β-arylvinyl)tropylium ions, namely β-(1-naphthyl)- (IX), β-(2-naphthyl)- (X), and β-(9-anthryl), vinyltropylium (XI), ions[29], consitutes an exception. Although these ions have a longer conjugated π-electron system, their acidity is enhanced (the pK_S values are lower) compared with the stability of the styryl-

TABLE 2.

Acid	K_{diss} (in water)
Benzoic	$6 \cdot 10^{-5}$
Cinnamic	$4 \cdot 10^{-5}$
Phenylpropiolic	$6 \cdot 10^{-3}$

tropylium ion (pK_S = 4.13) and even the unsbustituted tropylium ion (pK_S = 4.01):



The acidity of tropylium ions of type (C) changes with the nature of the condensed rings, their number, and position. All six benzotropylium ions known at the present time exhibit greater acidity than the tropylium ion. The pK_a values for benzotropylium ions measured in sulphuric acid are listed in Table 3.

The increase of the acidity (decrease of pK_a) of the tropylium cation condensed with benzene rings is surprising at first sight, since it might have been supposed that in such compounds the positive charge would be more delocalised than in the unsubstituted tropylium ion. However, as already mentioned on p. 735, in the examination of the effect of the substituent on the acidity of the carbonium ion account must be taken of the effect of the substituent both on the cation R^+ and on the pseudobase ROH conjugated with it:

$$R^+ + 2\,H_2O \rightleftarrows ROH + H_3O^+ .$$

Probably the benzene rings condensed with the tropylium ion stabilise the uncharged cycloheptatriene system to a greater extent than the positively charged tropylium ring. This results in a decrease of pK_a. Heilbronner and coworkers[18] calculated the difference between the delocalisation energies of the cation E_{R^+} and the pseudobase E_{ROH}, denoted by A^+_{opt} (the energy of atomic delocalisation), for compounds (XII)–(XVIII):

$$A^+_{opt} = E_{R^+} - E_{ROH} .$$

They believe that the entropy and solvation effects and the change in hybridisation are the same for these compounds, i.e. on going from compound (XII) to (XIII), etc. only A^+_{opt} changes. On this basis, it is to be expected that the values of A^+_{opt} are related linearly to the pK_a. The authors showed that such a relation does indeed exist for the cations (XII), (XIII), (XV), (XVI), and (XVII) (see Fig. 2).

The breakdown of coplanarity in the cations (XIV) and (XVIII) leads to a higher acidity of the cation, compared with the values calculated from the plot in Fig. 2.[30]

In contrast to tropylium cations with condensed benzene rings, the tropylium ion condensed with a thiophen ring (XIX) is much more stable than the unsubstituted tropylium

TABLE 3.

(XII)	(XIII)	(XIV)	(XV)	(XVI)	(XVII)	(XVIII)
+4.7[2]	+1.7±0.1[15]	−2.9±0.3[16]	−1.9±0.1[17]	+2.2±0.1[18]	+0.3±0.1[16]	−7.4[19]

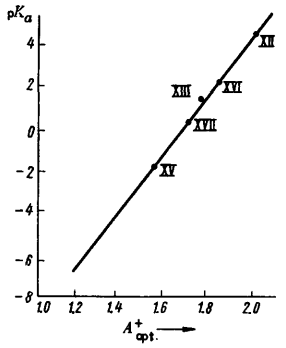
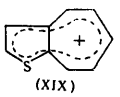


Fig. 2. Variation of the pK_a values for benzotropylium ions with the atomic delocalisation energy A^+_{opt}.

ion[31]: the pK_a value for this cation is +6.05 (pK_a = +4.75 for the tropylium ion).



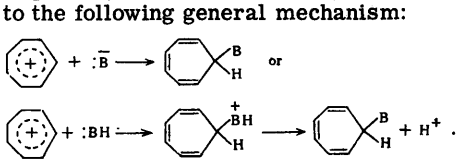
(XIX)

Thus the introduction of the substituent linked to the tropylium ring by a single σ-bond [ions of types (A) and (B)] alters the acidity of the cation in a manner depending on the electron-donor or electron-acceptor properties of the substituent. Electron-donor substituents reduce the acidity of the tropylium ion and electron-acceptor substituents increase it. The explanation of this is probably that such substituents have a much greater effect on the positively charged seven-membered tropylium ring than on the uncharged cycloheptatriene system. On the other hand, in cations of type (C), for example the benzotropylium ion, the condensed benzene rings stabilise the cycloheptatriene system to a greater extent than the tropylium system, and this has been confirmed by calculations. This leads to an increase of the acidity of the benzotropylium ions, i.e. a decrease of their pK_a values, compared with the unsubstituted tropylium ion.

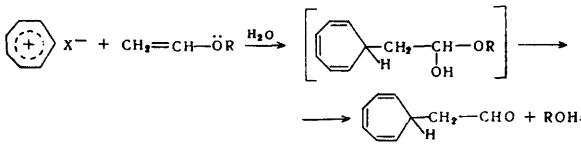
III. REACTIONS WITH TRANSFER OF ELECTRONS TO THE TROPYLIUM ION

1. The Tropylium Ion as the Acceptor in Charge-Transfer Complexes

As already mentioned, the tropylium cation is one of the most stable carbonium ions and it therefore constitutes an excellent model for the investigation of the properties of carbonium ions. The positive charge of the tropylium ion is responsible for its intense electron-acceptor properties, as in other carbonium ions. Thus the tropylium ion readily reacts with nucleophilic agents, for example with complex alkali metal hydrides[32], alkoxides, organometallic compounds, potassium cyanide, ammonia[2,9], etc. according to the following general mechanism:



The tropylium ion reacts readily also with compounds containing a double bond activated by electron-donor substituents, for example with vinyl ethers[33]:



The electron-acceptor properties of the tropylium ion are not shown only in their capacity to add to reaction centres at which there is an enhanced electron density, with formation of a covalent bond. In some cases the tropylium ion can form charge-transfer complexes, playing the role of the acceptor.

Usually the formation of a charge-transfer complex is detected from the appearance in the absorption spectra of new bands which are not characteristic either of the donor or the acceptor separately in the same solvent; this is accompanied by a deepening of the colour. McConnel[34] showed that the charge-transfer energy $E_{ct} = h\nu$ is linearly related to the ionisation potential of the donor and the electron affinity of the acceptor. The ionisation potentials or the electron affinities can be measured, for example by polarography; if there is a linear relation between the observed wavelengths of the maxima in the absorption spectra and the ionisation potentials, the formation of charge-transfer complexes is demonstrated. Such a linear relation has been obtained experimentally in a number of cases[35].

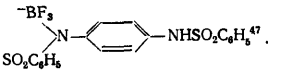
Charge-transfer complexes with the tropylium ion as the acceptor were observed for the first time by Feldman and Winstein[36]. They found that, when aromatic hydrocarbons are added to solutions of tropylium perchlorate and fluoroborate in dichloroethane and acetonitrile, new absorption bands, which are not characteristic either of the hydrocarbons or of the tropylium ion, appear in the ultraviolet and visible spectra (Table 4).

The observed wavelengths of the absorption bands are linearly related to the wavelengths of the absorption maxima of the charge-transfer complexes formed by the same donors with other acceptors, for example trinitrobenzene, iodine, or tetracyanoethylene. The energies of charge transfer from benzene, naphthalene, and anthracene to the tropylium ion have been calculated by the molecular orbital method as $E = h\nu = 1.445\beta$, 1.063β, and 0.859β respectively[1], whence λ_{max} = 322, 438, and 540 nm. The calculated data are in good agreement with those found experimentally (Table 4). On the basis of these results, the authors attributed the new absorption bands to charge transfer complexes of the tropylium ion and the aromatic hydrocarbons.

The tropylium ion forms charge-transfer complexes also with other donors, for example with certain anions.

As already stated above, the tropylium ion combines with certain nucleophilic species, in particular anions, with formation of a covalent bond. Highly nucleophilic ions give rise to a covalent bond, while weakly nucleophilic anions form ionic bonds with the tropylium ion. Vol'pin et al.[37] showed that the transitions from ionic tropylium compounds $C_7H_7^+X^-$ to covalent cycloheptatriene derivatives C_7H_7X occurs in the range of the K_a values of the corresponding acids between 1.2×10^{-4} (HNCO) and $(6.3-7.75) \times 10^{-5}$ (C_6H_5COOH and CH_3COOH), i.e. acids with $K_a > 1.2 \times 10^{-4}$ form ionic compounds with the tropylium ion, while those with $K_a < 6.3 \times 10^{-5}$ form covalent compounds.

A large number of ionic tropylium compounds are known at the present time, namely salts with the following anions: Br^-, Cl^-, I^-, BF_4^-,[38] SiF_6^-, ClO_4^-, $PtCl_6^{2-}$, $B(C_6H_5)_4^-$, HgI_4^{2-}, $HgBr_4^{2-}$,[3] BCl_4^-, BBr_4^-, BI_4^-,[39-43] HCl_2^-, HBr_2^-,[44] $SnCl_6^{2-}$,[45] $SnBr_6^{2-}$, $AlCl_4^-$, $FeCl_4^-$,[46]



Their ultraviolet spectra, polarographic behaviour, and magnetic properties as well as X-ray diffraction studies show[3] that all these compounds contain the same cation $C_7H_7^+$. Thus there is now no doubt about the capacity of the tropylium ion to form ionic bonds with certain anions. However, some anions are capable of forming charge-transfer complexes with the tropylium cation under certain conditions.

Doering[8] explained the colour of tropylium halides by the formation of charge-transfer complexes. Kitaigorodskii et al.[4] pointed out the possible presence of a weak charge-transfer bond between the seven-membered ring and the iodide anion in crystalline tropylium iodide. Harmon and coworkers showed[48,49] that the absorption spectra of tropylium halides in methylene chloride (a solvent with a low dissociation capacity and a dielectric constant ϵ = 9.08) contain new bands, compared with the spectra of tropylium halides in sulphuric acid, for example (Table 5).

In contrast to the halides, the solutions of tropylium perchlorate and fluoroborate are not coloured and do not show absorption bands in the long-wavelength region. The halide solutions retain their colour only when fresh and therefore the colour is not due to decomposition products or polarisation, as sometimes happens. The wavelengths of the maxima in the absorption spectra are linearly related to the ionisation potentials of the anions.

On the basis of the results obtained, Harmon et al.[48,49] concluded that in solution in methylene chloride the tropylium ion forms charge-transfer complexes (CTC) with halide anions. Such complexes are not formed with the anions BF_4^- and ClO_4^-. In more polar solvents the absorption bands due to charge transfer disappear. This is consistent with the properties of other charge-transfer complexes, the positions of the absorption maxima of which depend on the polarity of the solvent. Kosower showed

TABLE 4.

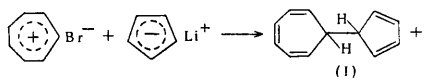
Hydrocarbon	λ_{max} in $ClCH_2CH_2Cl$, nm	λ_{max} in CH_3CN, nm	Hydrocarbon	λ_{max} in $ClCH_2CH_2Cl$, nm	λ_{max} in CH_3CN, nm
Benzene	305	—	Naphthalene	430	395
Toluene	325	310	2-Methylnaphthalene	472	—
m-Xylene	—	330	Phenanthrene	425	—
p-Xylene	340	323	Anthracene	530	487
Mesitylene	365	350	Pyrene	535	—

TABLE 5.

Salt	$C_7H_7^+Cl^-$	$C_7H_7^+Br^-$	$C_7H_7^+I^-$
λ_{max} (additional) in CH_2Cl_2, nm	293	402	422

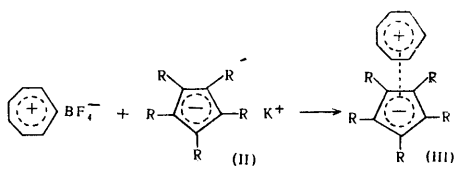
that the dependence of the position of the maxima in the absorption spectra of charge-transfer complexes on the nature of the solvent is represented by a straight line when a special quantity Z characterising the polarity is introduced[50]. It was found that the energy of charge transfer for tropylium iodide in various solvents is also linearly related to Z (Fig. 3)[51].

Thus halide anions occupy a middle position among other anions as regards their nucleophilic properties: they form ionic compounds with the tropylium ion but they are sufficiently nucleophilic to give rise also to a charge-transfer complex. It is reasonable to expect that certain organic anions forming a covalent bond with the tropylium ion may form charge-transfer complexes with the tropylium ion when electron-acceptor substituents are introduced into the anions. In fact, on interaction with the tropylium ion, lithium cyclopentadienide forms a covalent compound—(1-cyclopentadienyl)cycloheptatriene[37]:



(I)

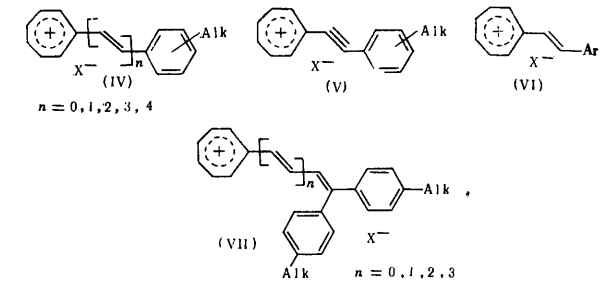
In contrast, LeGoff and La Caunt[52] showed that with potassium 1,2,3,4,5-pentamethoxycarbonylcyclopentadienide the tropylium ion forms a salt-like compound (III), with an absorption maximum in the region of 470 nm, which is not characteristic of the individual ions, i.e. a charge-transfer complex forms:



(II) (III)

where R = $COOCH_3$.

In the cases described the tropylium ion is the acceptor, while the donors are either hydrocarbon molecules or anions. However, Jutz showed that substituted tropylium cations (IV)–(VII), with substituents having a mobile π-electron system, also exhibit certain properties characteristic of charge-transfer complexes[24,27-29]. Jutz calls these cations "internal" charge-transfer complexes, in which the tropylium ring is the acceptor and the substituent is the donor:



(IV) (V) (VI)

$n = 0, 1, 2, 3, 4$

(VII)

$n = 0, 1, 2, 3$

where Ar = phenyl, 1-naphthyl, 2-naphthyl, 9-phenanthryl, 3-pyrenyl, and 9-anthryl and X = ClO_4 and BF_4. In fact all these salts are coloured (they absorb in the long-wavelength region of the spectrum). All the cations (IV)–(VII) are characterised by negative solvatochromism (displacement of the absorption maxima into the long-wavelength region on going to less polar solvents), which is shown mainly in the long-wavelength absorption maxima. Electron-donor substituents have a powerful effect on the positions of these absorption maxima, displacing them towards longer wavelengths. Furthermore, Jutz showed that for the cations (VI) there is a linear relation between the energies $E = h\nu$ (for the long-wavelength maxima) and the ionisation potentials $E_{1/2}$ of methyl-substituted hydrocarbons corresponding to the substituents[24,27-29,53]. Consequently interaction of the donor–acceptor type takes place in charge-transfer complexes between the tropylium ring and the substituents in the cations (IV)–(VI).

Thus the tropylium ion can form ionic and covalent bonds and also donor–acceptor bonds in charge-transfer complexes. The latter are of great theoretical interest, since they are logical intermediates in reactions involving nucleophilic addition to carbonium ions, both stable and transient, which are formed in many reactions.

2. Electron Transfers to the Tropylium Ion

In the discussion of charge-transfer complexes as intermediates in reactions it is assumed that the first stage of the reaction is displacement of electron density, while the interchange of nuclei and their fixation in new positions constitute a secondary process[54]. However, one could imagine that in some cases the displacement of electron density may be followed by electron transfer without displacement of the nucleus. In the case of the tropylium ion the tropyl radical C_7H_7 or its dimerisation product (ditropyl) should then form. The possibility of such chemical reactions with the tropylium ion is confirmed by the high conjugation energy of the tropyl radical, which, according to Streitwieser's calculations[55], is -2.54β, and also by the low potential of the one-electron electrochemical reduction of the tropylium ion, which is 1.2 V§.[56]

In fact, Doering[9] showed that ditropyl forms in the interaction between a tropylium salt and zinc dust in aqueous solution. According to Vol'pin's data[58], the

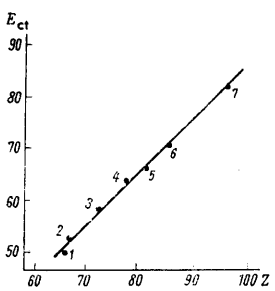
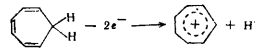


Fig. 3. Variation of the charge transfer energy E_{ct} of tropylium iodide in various solvents with the quantity Z characterising the polarity of the solvent:
1) methylene chloride; 2) acetone; 3) acetonitrile; 4) isopropyl alcohol; 5) ethyl alcohol; 6) methyl alcohol; 7) water.

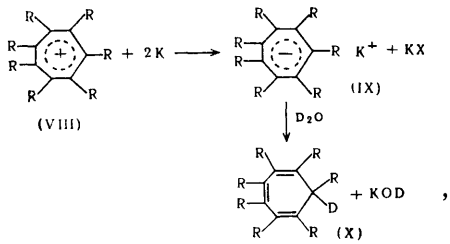
§ It is interesting to note that the tropylium ion forms in the electrochemical oxidation of cycloheptatriene, i.e. two-electron oxidation takes place[57]:



tropylium ion reacts similarly with other metals, even noble metals, i.e. tropyl behaves as a metal located on the right-hand side in the potential series. Probably tropyl radicals are formed in the reaction, and their dimerisation leads to the formation of ditropyl:

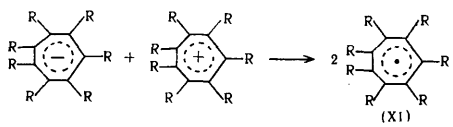


Indeed, under special conditions, namely when freshly sublimed tropylium bromide reacts with a sodium–potassium alloy in dimethoxyethane solution at −80°C, dos Santos-Veiga[59] succeeded in measuring the ESR spectrum of the tropyl radical. In some cases there is a possibility of the transfer of two electrons to the tropylium ring with the formation of a seven-membered anion. Thus Breslow and Chang[60,61] showed that the reaction of the heptaphenyltropylium ion (VIII) with metallic potassium leads to the formation of potassium heptaphenylcycloheptatrienide (IX), which is soluble in dimethoxyethane but insoluble in ethyl ether. In the reaction with D_2O there forms potassium hydroxide and deuterioheptaphenylcycloheptatriene (X), whose structure has been demonstrated by NMR spectroscopy:



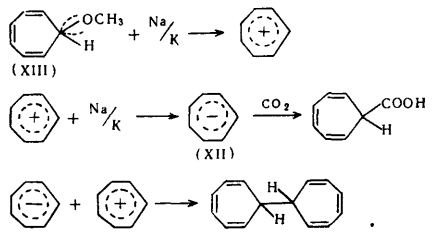
where R = C_6H_5.

When the anion (IX) reacts with an excess of a tropylium salt, there forms a radical (XI), which gives rise to an ESR signal (the anion does not exhibit paramagnetic properties):



where R = C_6H_5.

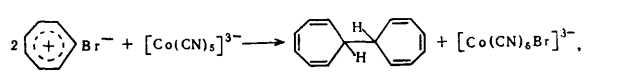
Dauben explained by a two-electron transfer the formation of the unsubstituted cycloheptatrienide anion (XII).[62] He showed that, when methoxycycloheptatriene (XIII) is added slowly to a solution of the sodium–potassium alloy in tetrahydrofuran at −20°C, a blue solution forms, whose subsequent carboxylation yields ditropyl and cycloheptatriene-7-carboxylic acid, which is evidence of the formation of the anion as an intermediate. Dauben suggests the following reaction mechanism:



The C–O bond in methoxycycloheptatriene undergoes ionic dissociation with formation of the tropylium ion, which is further reduced by the alkali metal to the anion, yielding on carboxylation cycloheptatrienecarboxylic acid¶. One-electron transfer from the anion to the tropylium ion yields ditropyl.

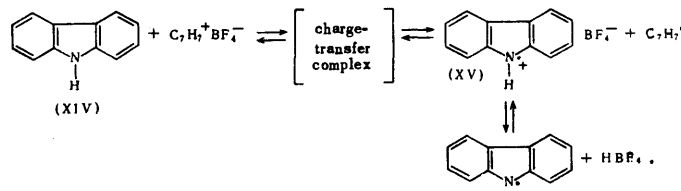
It is noteworthy that Bauld and Brown[63] succeeded in demonstrating with the aid of ESR spectroscopy that during this reaction there is a possibility of the transfer of yet another electron to the cycloheptatrienide anion with the formation of a radical-dianion.

The tropylium ion may be reduced to ditropyl by transition metal complexes, for example[64]:

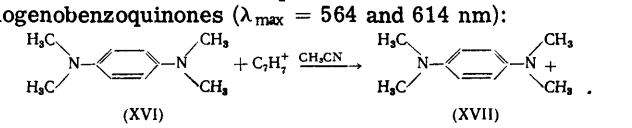


$NaMn(CO)_5$, $KFe(CO)_nH$, $HgFe(CO)_n$,[65] $V(CO)_6$, and $Na[C_5H_5Cr(CO)_3]$[66] have a similar effect on the tropylium ion.

Ledwith and coworkers[67,68] showed that the tropylium ion can remove electrons from certain heterocyclic compounds containing a double bond or an aromatic ring. The latter form radical cations on giving up an electron. Thus carbazole (XIV) is oxidised by the tropylium ion to the radical-cation (XV), whose structure has been demonstrated by NMR, infrared, and ESR ($g \simeq 2$) spectroscopy.

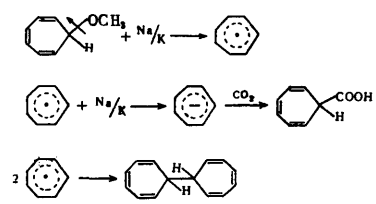


The radical-cation (XV) contains a labile hydrogen atom, as a result of which it is unstable. When *N*-methylcarbazole was used, a radical-cation stable in neutral solution was obtained. To confirm the occurrence of one-electron transfer to the tropylium ion, *NN*-tetramethyl-*p*-phenylenediamine (XVI), which is known to form radical-cations with other acceptors, for example halogenobenzoquinones[69], was used as the reducing agent. It was found that in the reaction with the tropylium ion it forms a radical-cation (XVII) which is identical with that produced in the reaction with halogenobenzoquinones (λ_{max} = 564 and 614 nm):



Unfortunately, in none of their experiments did the authors isolate ditropyl, whose formation would constitute important evidence of the occurrence of one-electron transfer to the tropylium ion.

¶ Although heterolytic dissociation of the C–O bond in cycloheptatriene derivatives under the action of electrophilic agents is widely known in the chemistry of the tropylium ion, we believe that in this case one cannot entirely exclude the possibility of homolytic dissociation:



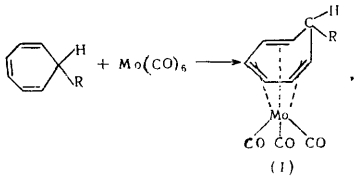
Thus the electron-acceptor properties of the tropylium ion, which is a carbonium ion, are shown not only in its capacity to combine with a species having an electron pair, but also in its capacity to combine with electrons. One-electron transfer to the tropylium ion leads to the formation of the tropyl radical or its dimer and two-electron transfer leads to the formation of the cycloheptatrienide anion. Systems with less mobile electrons can form charge-transfer complexes with the tropylium ion.

IV. SANDWICH COMPOUNDS OF THE TROPYLIUM ION

Sandwich compounds of transition metals with cyclopentatrienyl and arene ligands are widely known at the present time. Many studies have been made on their synthesis and properties. The sandwich compounds of transition metals in which the ligands are C_7H_7 rings have been almost not investigated.

Like the cyclopentadienyl and benzyl rings, the cycloheptatrienyl ring has six π-electrons which can form a bond with a central metal atom. Physical measurements, namely X-ray diffraction analysis and NMR and infrared spectra, have shown that, as a rule, all the carbon atoms of the cycloheptatrienyl ring are identical and lie in one plane. On this basis, one can postulate that the seven-membered ring in such complexes has the structure of the tropylium ion and the complexes may be regarded as tropylium complexes of transition metals.

Attempts to obtain transition metal complexes with the tropylium cation were made soon after its synthesis by Doering[2]. Wilkinson[65,70] was the first to attempt the preparation of a tropylium complex of this kind. In the reaction of a metal carbonyl with cyclopentadiene or benzene three carbonyl groups are capable of being replaced by the cyclopentadienide or benzene system, hydrogen being removed from cyclopentadiene in the reaction with the latter. Wilkinson hoped that in the reaction between cycloheptatriene and molybdenum hexacarbonyl the carbonyl group would also be replaced by the tropylium aromatic system with simultaneous removal of the hydrogen atom. However, the latter did not occur and Wilkinson obtained cycloheptatrienemolybdenum tricarbonyl (I). The reaction with cycloheptatriene derivatives took place similarly:

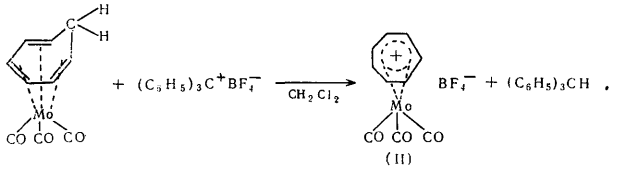


(I)

where R = H, C_6H_5, C_7H_7, OC_7H_7.

The attempts to prepare the desired complex by introducing tropylium bromide directly into the reaction were also unsuccessful.

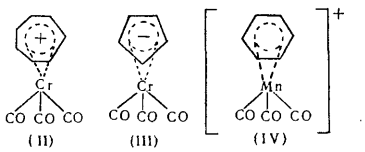
Dauben succeeded in preparing a tropylium complex[71]. Before this he established that, when salts of the triphenylmethyl cation are allowed to act on cycloheptatriene and its derivatives, a hydride ion migrates from cycloheptatriene to the carbonium ion with formation of a tropylium salt and triphenylmethane[38]. An analogous reaction with the cycloheptatrienemolybdenum tricarbonyl obtained by Wilkinson would yield tropylium-molybdenum tricarbonyl (II). The reaction did indeed take place, and the required complex (II) was obtained in quantitative yield:



(II)

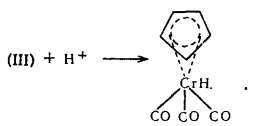
Compound (II) is more symmetrical than the cycloheptatriene complex (I). The greater symmetry of compound (II) is shown in the fact that the infrared spectra have only two carbonyl maxima, analogous to the absorption maxima of cyclopentadienylmanganese tricarbonyl and benzenechromium tricarbonyl, while three carbonyl maxima are observed in the spectrum of the cycloheptatriene complex. NMR spectra reveal the presence of protons of only one type, which confirms the highly symmetrical structure of the complex, with the metal atom bound to all seven carbon atoms of the seven-membered ligand. Complexes with chromium and tungsten were obtained similarly[72,73].

Pauson compared the sandwich cations obtained by Dauben with charged complexes of the type of cyclopentadienylchromium tricarbonyl (III) and benzenemanganese tricarbonyl (IV):[74]

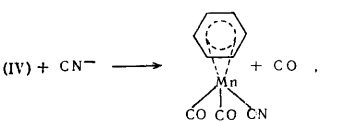


(II) (III) (IV)

Pauson believes that the negative charge in complex (III) is mainly localised in the ring although it is reduced by the action of the electron-acceptor group $M(CO)_3$. However, the addition of a positively charged species to the ring† would lead to the breakdown of the inert-gas electron shell of the system as a whole. Therefore the addition of an electrophilic agent, for example a proton, to the metal atom with formation of a carbonyl hydride is energetically more favourable:

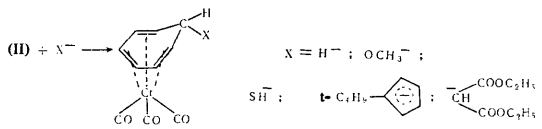


As a result of the same factors as those postulated for compound (III), the positive charge in complex (IV) is distributed between the benzene ring and the metal and again there is no addition of a nucleophilic species to the ring. However, in contrast to compound (III), a nucleophilic species does not add to the metal atom either, since manganese does not have vacant orbitals and therefore reaction, with a cyanide ion for example, can take place only with displacement of a carbonyl group:



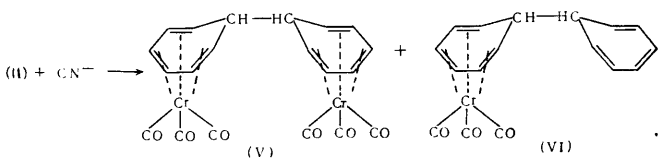
† In this and other cases where a species adds to a ligand or a metal atom only the final products are considered and not the reaction mechanism.

Pauson believes that, in contrast to these compounds, the tropylium complex (II) has a positive charge on the ring, the charge being enhanced further by the electron-acceptor effect of the $M(CO)_3$ group. The addition of nucleophilic species to the ring can result in this case in stable final products, due to the formation of a cycloheptatriene ring linked to the metal atom via six π-electrons, i.e. the inert-gas shell does not break down. In fact the cation (II) does react with certain nucleophilic agents, cycloheptatriene complexes being formed[75]:



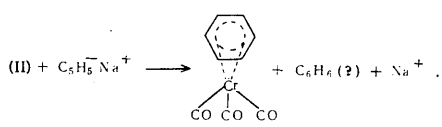
This reaction is analogous to the reactions of the free tropylium ion. Pauson called it the "normal" reaction of tropyliumchromium tricarbonyl salts with anions.

Apart from the "normal" reaction characteristic of the free tropylium ion, reactions characteristic of the system as a whole, with some similarities to those of other carbonyl complexes, were to be expected for complex (II). Pauson and Munro hoped to replace the carbonyl group by a cyanide ion, as happens in benzenemanganese tricarbonyl, already mentioned, and other complexes. However, the reaction of tropyliumchromium tricarbonyl with sodium cyanide takes place in a different manner. Apart from a small amount of the product of the "normal" addition, the authors isolated substances with structures (V) and (VI):[76]

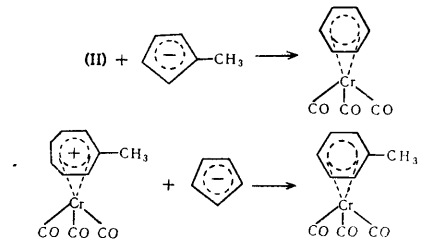


The reaction with $NaHCO_3$, CH_3COONa, $NaNH_2$, C_6H_5Li, $C_6H_5\overset{O}{\overset{\|}{C}}NH_2$, and HCl (2 *N*) takes place similarly. This process was called the "anomalous" reaction of complex (II) with anions.

Attempting nevertheless to replace the carbonyl groups in tropylium chromium tricarbonyl by a nucleophilic species, Pauson and Munro allowed the cyclopentadienide anion, which has a considerable affinity for the metal, to react with the complex. To their surprise, they failed to isolate after the reaction the products of either the "normal" or the "anomalous" addition. Instead they obtained benzenechromium tricarbonyl[73,77]:

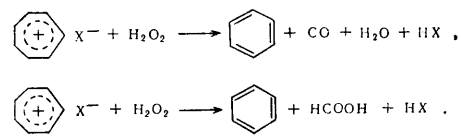


Benzenechromium tricarbonyl is also obtained in the reaction between tropyliumchromium tricarbonyl and sodium methylcyclopentadienide. On the other hand, the reaction between methyltropyliumchromium tricarbonyl and sodium cyclopentadienide results in the formation of toluenechromium tricarbonyl:



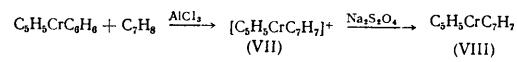
Thus benzene bound to chromium is obtained as a result of the contraction of the seven-membered ring of complex (II). To confirm this finding completely, the authors used in the reaction a tropylium complex labelled with tritium and indeed they observed the expected activity in the benzenechromium tricarbonyl. The contraction of the tropylium ring to the benzene ring in compound (II) was also found to occur in the reaction with sodiomalonic ester in the presence of an excess of the complex (in the presence of an excess of the sodiomalonic ester the reaction takes place with formation of "normal" addition products). Hence the authors concluded that the "normal" product forms first and then ring contraction takes place.

The rearrangement of the seven-membered ring to a six-membered ring with simultaneous elimination of one carbon atom is also known in the chemistry of free tropylium ions. Vol'pin et al. showed[78] that, when a dilute aqueous solution of hydrogen peroxide is allowed to act on the tropylium ion at room temperature, benzene in 80% yield, carbon monoxide, and formic acid are formed:

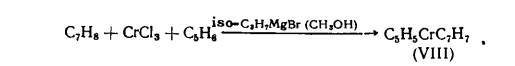


The "anomalous" addition reaction and the reactions involving the contraction of the seven-membered ring showed that the tropylium complexes obtained for the first time by Dauben are new systems, whose study is of great interest.

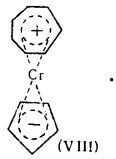
Apart from these complex cations, uncharged sandwich compounds of the tropylium ion have been described. If the three carbonyl groups in cycloheptatrienylchromium tricarbonyl are replaced by the cyclopentadienyl residue, the molecule will be uncharged as a whole. Such a complex (VIII) was obtained by Fischer from cyclopentadienylbenzenechromium and cycloheptatriene in the presence of aluminium chloride, with subsequent hydrolysis of the reaction mixture and the reduction with sodium hydrosulphite of the cation (VII) formed initially[79]:



Somewhat later King and Bisnette[80] obtained the same complex (VIII) by a more convenient method, involving the reaction of isopropylmagnesium bromide with a mixture of chromium trichloride, cyclopentadiene, and cycloheptatriene in ethereal solution at −78°C with subsequent alcoholysis of the reaction mixture:

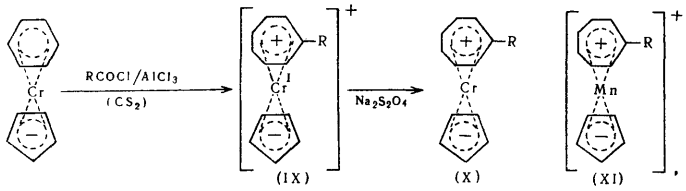


The NMR spectra of compound (VIII) revealed the presence of two types of protons in a ratio of 5 : 7. The infrared spectra also correspond to conjugated five- and seven-membered rings. The dipole moment is 0.79 D in benzene. On the basis of these data, and also in view of the tendency of the C_7H_7 and C_5H_5 systems to undergo conversion into the ions $C_7H_7^+$ and $C_5H_5^-$, a structure with partial positive and negative charges on the seven-membered and five-membered rings respectively may be put forward for compound (VIII):



(VIII)

Similar complexes with an unsubstituted tropylium ring were unexpectedly obtained by Fischer (in 10% yield) in attempts to acylate cyclopentadienylbenzenechromium by the Friedel–Crafts method[81]:



(IX) (X) (XI)

where R = CH_3 or C_6H_5. The cation (IX) formed initially yields on reduction the uncharged complex (X), which has an inert-gas electron shell. With manganese, which has in its shell one electron more than chromium, the tropylium cation (XI), with 18 π-electrons, forms immediately.

Both complexes have similar infrared spectra and the NMR spectra reveal three types of protons in ratios of 6 : 5 : 3 (for R = CH_3), which is consistent with structures (X) and (XI). To confirm the tropylium structure of the ligand, the authors, using Dauben's method, obtained from the cycloheptatriene complex a compound identical with compound (X).

The paramagnetic cycloheptatrienylcyclopentadienylvanadium, obtained by King and Stone[82] in the reaction between cycloheptatriene and cycloheptadienylvanadium tetracarbonyl:

$$C_5H_5V(CO)_4 + C_7H_8 \rightarrow C_5H_5VC_7H_7 ,$$

and also the diamagnetic cycloheptatrienylvanadium tricarbonyl[65] have structures similar to that of complex (X). The planarity of the seven-membered ring and its high symmetry have been demonstrated by X-ray diffraction measurements[83] and also by NMR and infrared spectroscopy[65,84].

The platinum complex (XII), obtained by Fischer and Fritz[85], is somewhat exceptional. The infrared spectra of this complex are very similar to those of tropylium bromide and differ markedly from the spectra of cycloheptatriene. On the basis of these data, the authors assert that the seven-membered ligand has the tropylium structure:

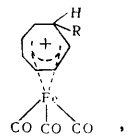
$$PtBr_4 + C_7H_8 \rightarrow (C_7H_7PtBr_2)_2 .$$

(XII)

Thus at the present time only synthetic methods and certain physical properties, which suggest a tropylium structure of the seven-membered ring, have been described for uncharged complexes with the seven-membered ligand.

So far tropylium complexes of transition metals in which an inert-gas electron shell was achieved (the paramagnetic cycloheptatrienylcyclopentadienylvanadium, which has one unpaired electron, is an exception) were considered. Metals of Group VIB then remain zerovalent, vanadium in tropylium vanadium tricarbonyl[65] has a valence of –1, and the cyclopentadienyltropylium-manganese complex[81] is a cation. Analogous complexes of iron, i.e. complexes with a tropylium ligand, for example $[C_7H_7Fe(CO)_3]^+$, would have two electrons more than the corresponding inert gas, or, if Sidgwick's rule holds, would be triply charged cations. Attempts have been made to synthesise such complexes and to determine their structure.

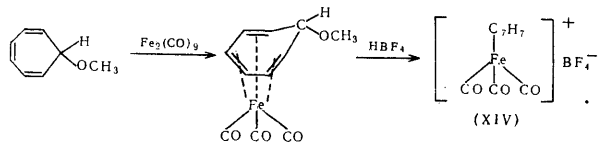
Dauben[72] tried to prepare a complex of iron and the C_7H_7 ligand in the reaction between the triphenylmethyl cation and cycloheptatrieneiron tricarbonyl. However, instead of the removal of a hydride ion, the carbonium ion added to the double bond of the cycloheptatriene ring with formation of the cation (XIII):



(XIII)

where R = $(C_6H_5)_3C$.

It appears that Pettit and coworkers[86] succeeded in obtaining the desired complex $[C_7H_7Fe(CO)_3]^+BF_4^-$ (XIV) by the action of methoxycycloheptatriene on iron carbonyl with subsequent decomposition with acid of the methoxycycloheptatrieneiron tricarbonyl produced:



(XIV)

However, the study of the chemical properties of compound (XIV) suggests that the ligand C_7H_7 is more likely to have the tropylium structure. Indeed hydrolysis of complex (XIV) yields a complex of tropyl alcohol $C_7H_7OHFe(CO)_3$. Acid decomposition of the latter again results in the formation of compound (XIV). A similar reaction also occurs in the chemistry of the free tropylium ion:

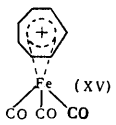
$$C_7H_7^+ + H_2O \rightleftharpoons C_7H_7OH + H^+ .$$

Only one signal is observed in the NMR spectra of complex (XIV), i.e. there is only one type of proton. This confirms the symmetrical tropylium structure of the ligand C_7H_7. However, the authors observed in the infrared spectra three absorption bands in the region of C–H vibrations instead of one, as would be expected for the symmetrical C_7H_7 ligand. Comparison of the acidity constants of complex (XIV) and the free tropylium ion (Table 6) shows that the cation (XIV) is less stable than the tropylium cation, while the tropylium complexes of Group VIB metals are more stable than the tropylium cation itself.

TABLE 6.

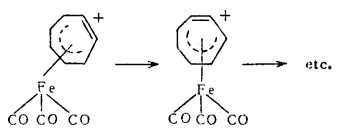
	pK_a in water		pK_a in water
(1) C_7H_7	+4.7	(4) $C_7H_7W(CO)_3$	+6
(2) $C_7H_7Cr(CO)_3$	+6.3	(5) $C_7H_7Fe(CO)_3$	+4.5
(3) $C_7H_7Mo(CO)_3$	+6.2	(6) $C_7H_9Fe(CO_3)$	+4.7

Therefore the structure of the tropylium complex (XIV) cannot be that of compound (XV):


(XV)

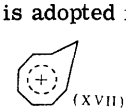
It follows from Table 6 that the pK_a values for the cations of cycloheptatrienyliron tricarbonyl (5) and cycloheptadienyliron tricarbonyl (6) are approximately equal. The study of the infrared spectra of the cation (XIV) showed that the vibrations of the carbonyl groups in this complex occur in the same region as the vibrations of the carbonyl groups in dienyliron tricarbonyl complexes (2070 cm^{-1} and 2120 cm^{-1}). Furthermore, the presence of an absorption band in the region of 731 cm^{-1} enabled the authors to suggest the presence of a *cis*-double bond.

On the basis of these results, Pettit and coworkers concluded that the cation (XIV) has the structure (XVI), analogous to that of cationic cyclopentadienyliron tricarbonyl, the inert-gas electron shell being achieved in complex (XVI):


(XVIa) (XVIb)

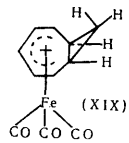
The identity of the protons revealed in the NMR spectra is explained by the rotation of the $Fe(CO)_3$ group about the seven-membered ring, which leads to the tautomers (XVIa), (XVIb), etc.

In conclusion we shall consider transition metal complexes with protonated cyclo-octatetraene as the ligand. Rosenberg et al.[87] showed that the NMR spectrum of free protonated cyclo-octatetraene $C_8H_9^+$ has four peaks with relative areas of 5 : 2 : 1 : 1. On this basis, the authors suggested that seven carbon atoms lie in one plane, forming a tropylium ring (this accounts for the stability of the cation), while the methylene group lies outside this plane. Thus the structure (XVII) is adopted for the cation $C_8H_9^+$.


(XVII)

Winstein and coworkers[88] found that the NMR spectra of the complex cation $[C_8H_9Mo(CO)_3]^+$ also reveal the presence of four types of proton in the ratios 5 : 2 : 1 : 1. Consequently the structure of the cation $C_8H_9^+$ [structure (XVII)] persists also in the complex (XVIII), which leads to the participation of six π-electrons in the formation of a metal–ligand bond and a stable common 18 π-electron shell. Thus the structure of protonated cyclo-octatetraenemolybdenum tricarbonyl (XVIII) resembles closely that of tropyliummolybdenum tricarbonyl.

Different workers have attributed different structures to the analogous iron complex[89,90]. Very recently Winstein and coworkers[88] showed, on the basis of a thorough study of the NMR spectra of protonated cyclo-octatetraeneiron tricarbonyl, that this complex has the structure (XIX), similar to the structure of dienylirion tricarbonyl, as for the complex $[C_7H_7Fe(CO)_3]^+$ [complex (XVI)]:


(XIX)

Complexes with the ligand C_7H_7 are now known for metals of Groups VB, VIB, VIIB, and VIII, examples being vanadium (Group V), chromium and molybdenum (Group VI), manganese (Group VII), and iron and platinum (Group VIII). In all these complexes, except for the iron complex, the seven-membered ligand has the tropylium structure and almost all the complexes obey Sidgwick's rule. Exceptions are the paramagnetic cycloheptatrienylcyclopentadienylvanadium $C_7H_7VC_5H_5$, the electron shell of which consists of 17 π-electrons, and the platinum complex $(C_7H_7PtBr_2)_2$, which probably has a shell consisting of 20 π-electrons. In the iron complex (XVI) four π-electrons form a metal–ligand bond of the type which exists in diene complexes and a shell of 18 π-electrons is formed.

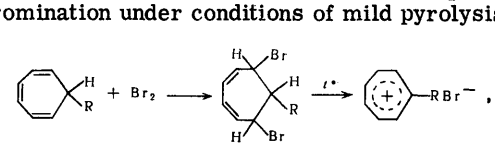
There are virtually no data at the moment concerning the reactivity of these complexes. Only certain reactions of the tropyliumchromium tricarbonyl cation are known[75-77]. The chemical properties of the uncharged complexes have not been investigated at all. It is not possible as yet to predict their behaviour in reactions, since the distribution of electron density, which is primarily responsible for chemical reactions, cannot be measured by methods available at the present time, and calculations yield very ambiguous answers (as shown by the calculation for the ferrocene molecule).[91,92] Nevertheless, there is no doubt that further studies will lead to interesting and unexpected reactions of these complexes, a feature which is characteristic of the chemistry of the sandwich compounds of transition metals in general.

V. FORMATION OF THE TROPYLIUM ION AND ITS PROPERTIES

1. Formation of the Salts of Substituted and Unsubstituted Tropylium Ions

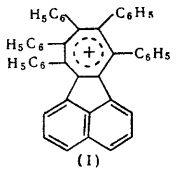
One of the characteristic properties of aromatic systems is known to be the ease of their formation. This applies also to the tropylium cation. The ways in which substituted and unsubstituted tropylium ions are formed are presented below.

1. Doering's method[2] consists in the bromination of cycloheptatriene and its derivatives with subsequent dehydrobromination under conditions of mild pyrolysis:



where R = H, COOH, C_6H_5, t-C_4H_9, and Br. Salts of carboxytropylium[20,93,94], phenyl-, t-butyl-, and bromotropylium[8], and also heptaphenyltropylium[25], and

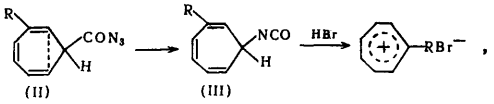
7,8,9,10,11-pentaphenylcyclohepta-acenaphthenylium[95] ions (I):



(I)

were obtained by this method.

2. The method of Dewar and Pettit[96,97] consists in heating the azides of norcaradienecarboxylic acid (II) in benzene with subsequent treatment of the resulting isocyanate (III) with hydrogen bromide:

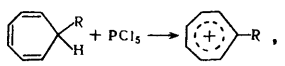


(II) (III)

where R = H and CH_3.

3. The removal of a hydride ion from cycloheptatriene derivatives.

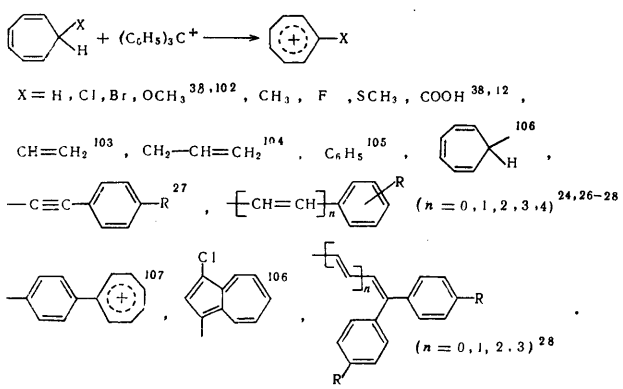
a. In the method of Kursanov and Vol'pin[98] the hydride ion is removed from cycloheptatriene and its derivatives with phosphorus pentachloride in an inert solvent. Salts of methyltropylium[98,99], and ethyl- and benzyl-tropylium[99]‡ ions have been obtained by this method from the 7-substituted cycloheptatrienes:



where R = H, CH_3, C_2H_5, and $CH_2C_6H_5$.

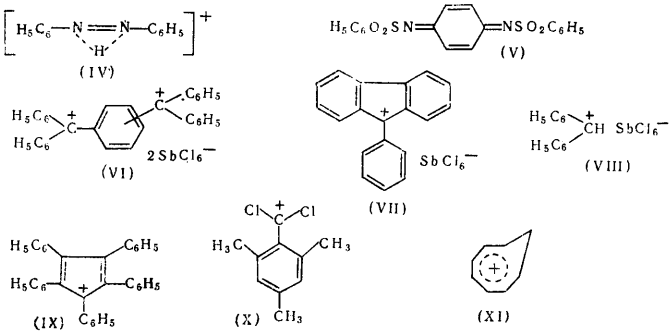
Salts of methoxy- and ethoxy-tropylium ions were obtained in the reaction of phosphorus pentachloride with 1-, 2-, and 3-alkoxycycloheptatriene[100]. When phosphorus pentachloride acts on 7-alkoxycycloheptatriene, the latter decomposes with formation of salts of the unsubstituted tropylium ion (cf. the results of Vol'pin and Akhrem[101]).

b. In Dauben's method[38] the hydride ion is removed from cycloheptatriene and its derivatives by the triphenylmethyl cation which results in the formation of triphenylmethane and an unsubstituted or substituted tropylium ion, which is a more stable carbonium ion than the triphenylmethyl cation:



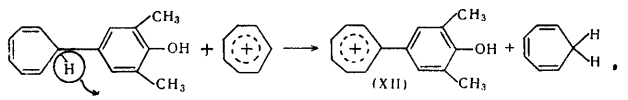
‡ The salts of ethyl- and benzyl-tropylium ions were not isolated in a pure form; a suspension of these salts in methylene-chloride was introduced directly into further reactions.

The following new acceptors have been used in recent years for the removal of the hydride ion from cycloheptatriene: protonated azobenzene (IV)[108,109], benzoquinones[110] and their derivatives, for example *p*-benzoquinone-dibenzenesulphonimide (V) in the presence of boron trifluoride-ether[47] and a number of stable carbonium ions synthesised for the first time, i.e. (VI)[111], (VII)[112], (VIII)[113], (IX)[114], (X)[115], and (XI)[87]:



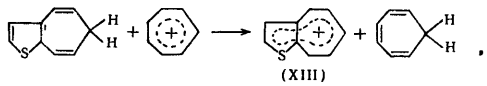
(IV) (V) (VI) (VII) (VIII) (IX) (X) (XI)

c. The removal of the hydride ions from cycloheptatriene derivatives under the action of the tropylium ion. In this case salts of a substituted tropylium ion more stable than those of the unsubstituted tropylium ion are formed. The 3,5-dimethyl-4-hydroxyphenyltropylium cation (XII)[116]:



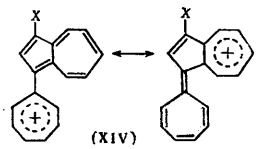
(XII)

the thenotropylium cation (XIII)[31]:



(XIII)

and the salts (XIV*a*) and (XIV*b*)[117]:

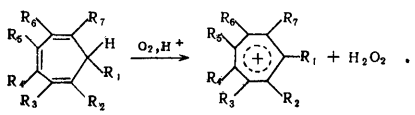


(XIV)

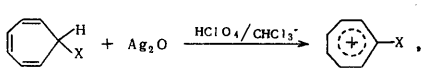
(X = H in *a* and X = C_7H_7 in *b*) were obtained in this way.

4. The oxidation of cycloheptatriene and its derivatives.

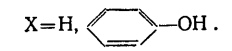
a. ter Borg et al.[118] showed that the oxidation of cycloheptatriene with atmospheric oxygen in acetic acid in the presence of perchloric or fluoroboric acids results in the formation of the tropylium ion in 30–70% yield. They suggest that substituted tropylium salts be obtained in a similar way[119]:



b. Nozoe[120] described the preparation of the tropylium and hydroxyphenyltropylium ions in the oxidation of cycloheptatriene and 4-cycloheptatrienylphenol respectively with silver oxide in chloroform solution in the presence of perchloric acid:

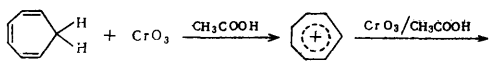


where

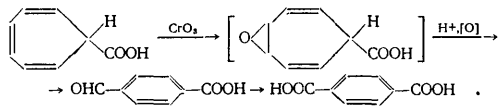


c. The oxidation of 7-cycloheptatrienecarboxylic acid (XV) with lead tetra-acetate, acid potassium permanganate, $Na_2S_2O_8$, $(NH_4)_2Ce(NO_3)_6$, and periodic acid also leads to the formation of the tropylium ion; in some cases benzaldehyde, benzyl alcohol, and terephthalic acid are formed at the same time[121].

In neutral and alkaline media potassium permanganate oxidises the acid (XV) to benzaldehyde and terephthalic acid. Doering showed that benzaldehyde forms in the oxidation of cycloheptatriene with chromic acid[9]. It also forms in the oxidation of the tropylium ion with chromic acid. On the basis of these data, Doering suggested that the oxidation of cycloheptatriene to benaldehyde takes place with the intermediate formation of the tropylium ion:



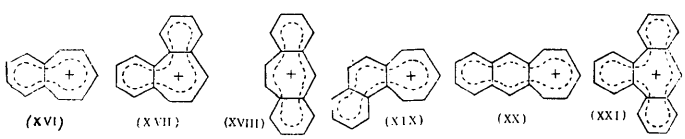
Juppé and Wolf[122] confirmed this reaction mechanism, by oxidising with chromic acid cycloheptatriene labelled with carbon-14 in the methylene group. They found that the benzaldehyde produced contains 6/7 of the label in the benzene ring. Dewar's ideas about the mechanism of the oxidation of cycloheptatriene-7-carboxylic acid to benzyl alcohol and benzaldehyde are consistent with Doering's hypotheses, but he proposes a different mechanism for the oxidation of the acid (XV) to terephthalic acid[121]:



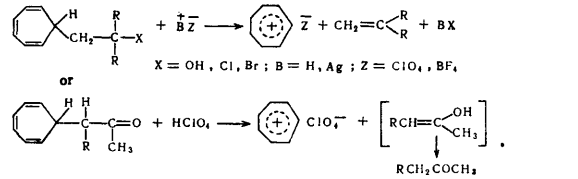
By oxidising cycloheptatriene with chromic anhydride in pyridine, Nozoe and coworkers obtained tropone[123]. The latter also forms in the interaction of the tropylium ion with the same oxidising agent. Using his own data and also the oxidation data described above, Nozoe was able to elucidate the mechanism of the oxidation of cycloheptatriene with intermediate formation of the tropylium cation.

5. Heterolytic dissociation of the bonds C–O, C–C, C–N, and C–S.

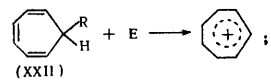
a. The C–O bond in tropylium ethers[2] and tropylium-carbinols is readily ruptured under the action of acids with formation of unsubstituted tropylium salts. When acids were allowed to act on the corresponding carbinols, benzotropylium (XVI)[15], dibenzo[*a*, *c*]tropylium (XVII)[16], dibenzo[*a*, *e*]tropylium (XVIII)[17], naphtho[2,1-*a*]tropylium (XIX)[18], naphtho[2,3-*a*]tropylium (XX)[16], and tribenzo[*a*, *c*, *e*]tropylium (XXI)[19] cations were obtained. The carbinols were produced by the reduction of the corresponding tropones with lithium aluminium hydride.



b. Under the action of electrophilic agents, the C–C bond in compounds with a carbonium centre in the β-position with respect to the cycloheptatrienyl residue may dissociate[3,124]:

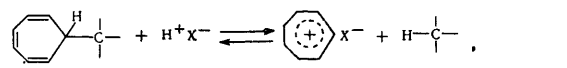


Recently Vol'pin and Akhrem showed[101] that this reaction is more general and is characteristic of cycloheptatriene derivatives with electron-acceptor substituents in the side-chain. Thus cycloheptatrienylmalonic acid (XXII*a*), cycloheptatrienylacetylacetone (XXII*b*), cycloheptatrienylacetaldehyde (XXII*c*) and cycloheptatrienylacetoacetic ester (XXII*d*) are cleaved by a wide variety of electrophilic agents E with formation of the tropylium ion:

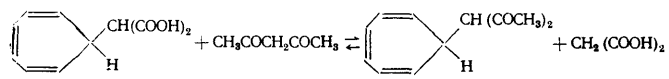


R = $CH(COOH)_2$ (*a*), $CH(COCH_3)_2$ (*b*), CH_2CHO (*c*), and $CH_2COOC_2H_5$ (*d*); E = Br_2, HCl(gas), HBr(gas), H_2SO_4, CH_3COOH, H_3PO_4, PCl_5, $(CH_3CO)_2O$, $(C_6H_5)_3C^+$, t-C_4H_9Br, $ZnCl_2$, and $FeCl_3$.

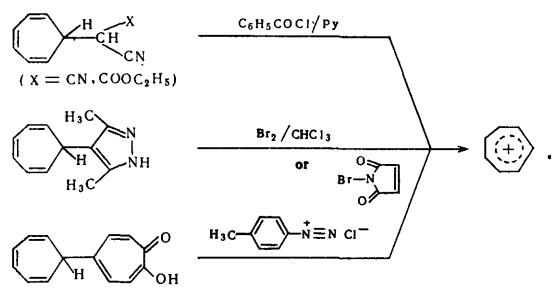
The authors suggested that this cleavage reaction is the reverse of the "tropylation" process[125]:



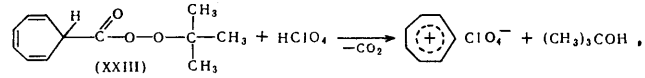
and confirmed this by the "transtropylation" reaction, which consists in the migration of the cycloheptatrienyl residue from one compound with a mobile hydrogen atom to another, for example,



Other examples of the dissociation of the C–C bond in cycloheptatriene derivatives with formation of the tropylium ion may be quoted[126–128]:

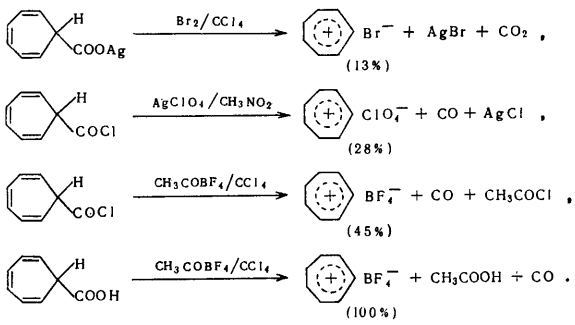


The tendency of cycloheptatriene to form the aromatic tropylium system is so great that under the action of a strong acid the C–C bond dissociates heterolytically even in the peroxide (XXIII)[129]:

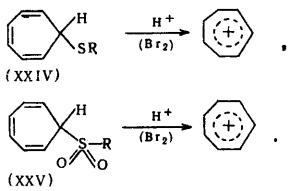


The following reactions of cycloheptatriene-7-carboxylic acid and its derivatives, proposed by Dewar and Ganellin[94]

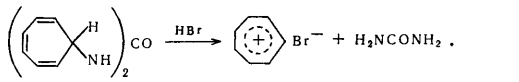
for the preparation of tropylium salts, may be included among processes involving the dissociation of the C–C bond in cycloheptatriene derivatives:



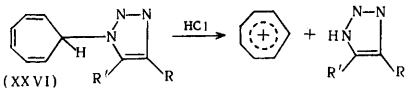
c. The C–S bond in thioethers (XXIV) and sulphones (XXV) of cycloheptatriene readily dissociates with formation of the tropylium ion under the action of acids, for example hydrobromic and perchloric acids or bromine in acetic acid[130,131]:



d. Doering showed, using ditropylurea as an example, that the C–N bond can also dissociate heterolytically with formation of the tropylium ion under the action of an acid[132]:

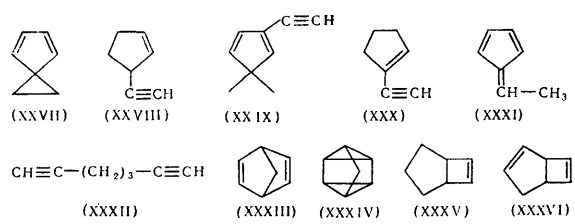


Recently Looker[133] described yet another case of the heterolysis of the C–N bond in cycloheptatriene derivatives (XXVI)[133]:



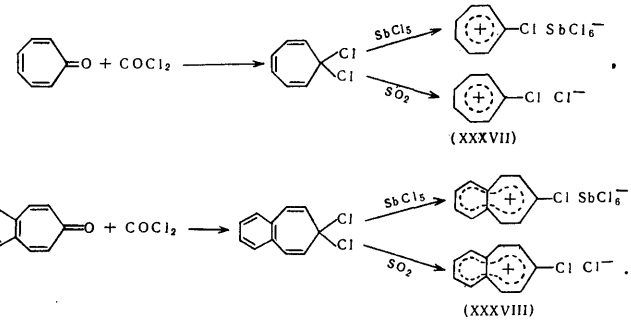
where R = R′ = $COOCH_3$, R = R′ = COC_6H_5 and R = CHO and R′ = H.

6. The formation of the tropylium ion in the mass spectrometer. Earlier it was shown that various alkylbenzenes form the tropylium ion on collision with electrons in the mass spectrometer[134]. In recent years a number of investigators have shown that benzyl chloride, benzyl alcohol[135], the isomeric C_7H_8 hydrocarbons (XXVII)–(XXXIV), cycloheptadiene, Δ^6-bicyclo[3,2,0]heptene (XXXV), and $\Delta^{2,6}$-bicyclo[3,2,0]heptadiene (XXXVI)[136–139] also have identical mass spectra:

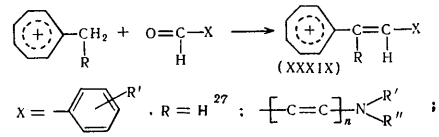


7. Other methods.

a. Föhlisch et al.[140] obtained the chlorotropylium (XXXVII) and 5-chloro-1,2-benzotropylium (XXXVIII) ions by the action of phosgene on tropone in sulphur dioxide or by further treatment with antimony pentachloride of the covalent dichloro-derivatives formed:

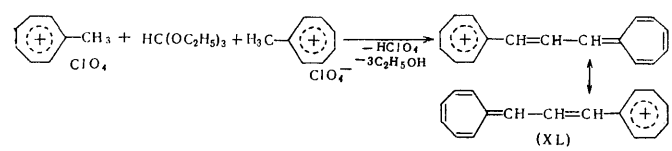


b. When methyl-, ethyl-, and benzyl-tropylium salts were condensed with aromatic aldehydes and their derivatives in acetic acid solution containing a small amount of perchloric acid, the following substituted tropylium compounds (XXXIX) were obtained:

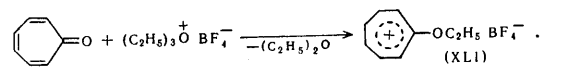


R = H, CH_3, and C_6H_5§ [38]; n = 0 and 1; X = 1-naphthyl, 2-naphthyl, 9-phenanthryl, 9-anthryl, and 3-pyrenyl; R = H.[29]

Hafner and coworkers obtained the salt (XL) by the condensation of the methyltropylium ion with orthoformic ester[141]:



By allowing tropone to react with triethyloxonium fluoroborate, they obtained ethoxytropylium fluoroborate (XLI):

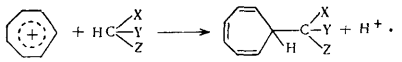


2. The Properties of the Tropylium Ion

The studies on the reactivity of the tropylium ion have continued in recent years. The most important property of the tropylium ion, as a carbonium ion, is its electrophilicity (see Section II). The tropylation reaction discovered by Vol'pin et al.,[142] i.e. the replacement of a mobile

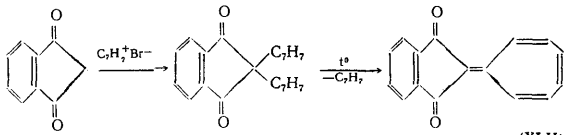
§ The interaction of methyl-, ethyl-, and benzyl-tropylium salts with N-substituted formamides and β-(dialkylamino) acrolein derivatives with formation of immonium salts takes place in the presence of phosphorus oxychloride.

hydrogen atom by the cycloheptatrienyl residue, is associated with the electrophilic properties of the tropylium ion:

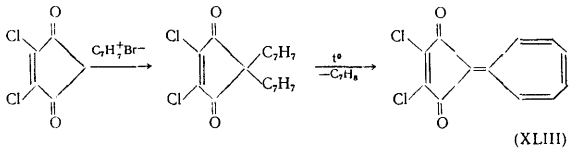


This reaction has found extensive application in the synthesis of cycloheptatriene derivatives.

Thus Jordan and Elliott [143] introduced the seven-membered ring into the molecules of 2-ethoxycarbonylcyclopentanone, potassium phthalimide, and indane-1,3-dione; Nozoe and coworkers introduced the seven-membered ring into β-naphthol [144] and tropolone [128], and Hafner [117] and later Anderson [106] "tropylated" azulene. Kitahara and coworkers obtained quinones of the sesquifulvalene series, (XLII) and (XLIII), with the aid of the tropylation reaction [145]:



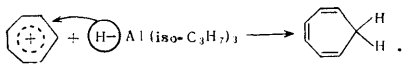
(XLII)



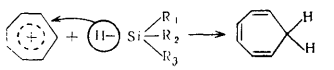
(XLIII)

Further examples of the reaction of tropylium ions in which a double bond is activated by electron-donor substituents, first observed by Vol'pin et al. [142,146], have been discovered [28,147].

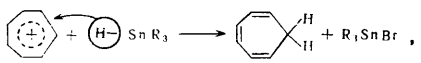
The tropylium ion as an acceptor of hydride ions has been used for the further study of hydride migrations. It has been shown that the tropylium ion can remove a hydride ion not only from complex alkali metal hydrides but also from simple aulminium hydrides [32]:



It has been found that the Si–H and Sn–H bonds can also dissociate heterolytically under the action of the tropylium ion [32,148]:

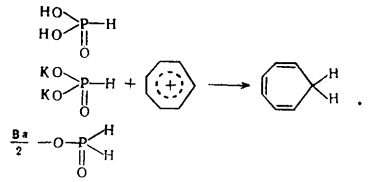


where $R_1 = R_2 = R_3 = C_2H_5$ and $R_1 = H$, $R_2 = CH_3$, and $R_3 = C_2H_5$.

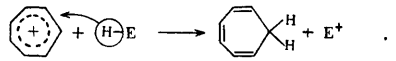


where $R = C_2H_5$ and C_6H_5.

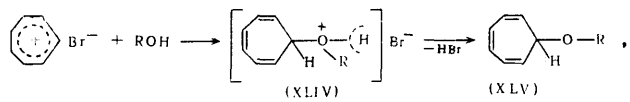
The study of the dissociation of the P–H bond under the action of the tropylium ion proved to be particularly interesting. Examples of both homolytic [149] dissociation of the P–H bond and ionic dissociation with the removal of a proton were known earlier [150]. Recently it has been shown that phosphorous acid, potassium phosphite, and barium hypophosphite in aqueous solution reduce the tropylium ion with formation of cycloheptatriene [10]:



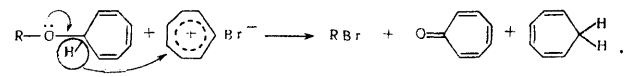
Thus it has now been demonstrated that heterolysis of an E–H bond with removal of a hydride ion under the action of the tropylium ion is in principle possible for elements of Groups I, III, IV, and V:



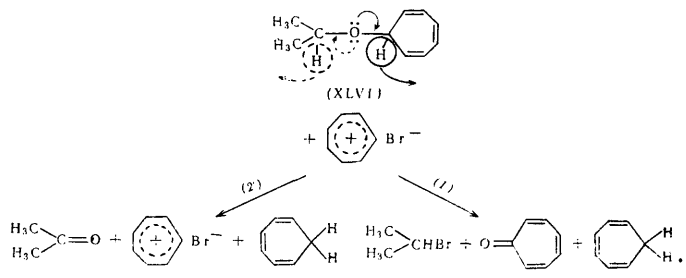
Systematic study of the interaction of the tropylium ion with alcohols has shown that the ion reacts with primary, secondary, and tertiary alcohols [151]. In the reaction with primary and tertiary aliphatic alcohols the first step is the formation of the hydroxonium compound (XLIV), which readily loses a proton with formation of the alkyl tropyl ether (XLV). The alkyl tropyl ether interacts with a second molecule of the tropylium salt. The tropylium ion then removes a hydride ion from the cycloheptatriene ring with formation of cycloheptatriene, tropone, and the alkyl halide:



(XLIV) (XLV)

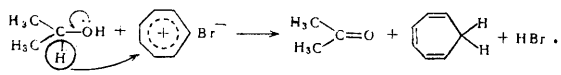


In the reaction with a secondary aliphatic alcohol, in particular isopropyl alcohol, acetone forms in addition to cycloheptatriene, tropone, and isopropyl bromide. The formation of acetone can be explained by the fact that in the reaction of the intermediate isopropyl tropyl ether (XLVI) with the tropylium ion a hydride ion may be removed not only from the cycloheptatriene ring (1) but also from the isopropyl group (2):



(XLVI)

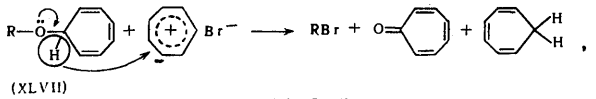
The authors showed that in the reaction between isopropyl ether and tropylium bromide a hydride ion is indeed removed both from the isopropyl group and from the cycloheptatrienyl ring. However, one cannot exclude the possibility of the direct removal of the hydride ion by the tropylium ion from the isopropyl alcohol molecule:



The occurrence of this process in the overall reaction can also be expected on the basis of the relatively large hydride mobility of the hydrogen atom in the CH group of isopropyl alcohol[152-156]. Similar considerations can also be used to explain the reaction between benzyl alcohol and the tropylium ion[32], as a result of which tropone is formed together with benzaldehyde and cycloheptatriene.

The high hydride mobility in alkyl tropyl ethers was suggested by the authors by analogy with the high hydride mobility of the hydrogen atom in ditropyl ether. Ter Borg and coworkers[157] and Nozoe and coworkers[158] showed that ditropyl ether is capable of interacting with the tropylium ion to form cycloheptatriene and tropone, catalytic amounts of the tropylium ion being sufficient for the reaction to occur[159].

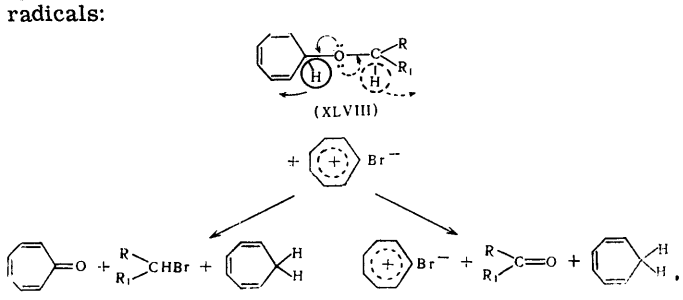
Alkyl tropyl ethers also react with the tropylium ion. In the reaction of methyl tropyl, n-propyl tropyl, and t-butyl tropyl ethers (XLVII) with the tropylium ion cycloheptatriene, tropone, and alkyl halides are formed. This is consistent with the hypothesis of the removal of a hydride ion from the seven-membered ring:



(XLVII)

where R = CH_3, n-C_3H_7, and t-C_4H_9.

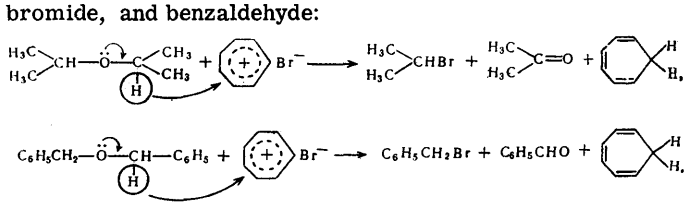
The reaction of isopropyl tropyl and benzyl tropyl ethers (XLVIII) with the tropylium ion results in the formation of acetone and benzaldehyde in addition to cycloheptatriene, tropone, and isopropyl and benzyl bromides. Thus in these processes a hydride ion is removed both from the cycloheptatriene ring and from the isopropyl and benzyl radicals:



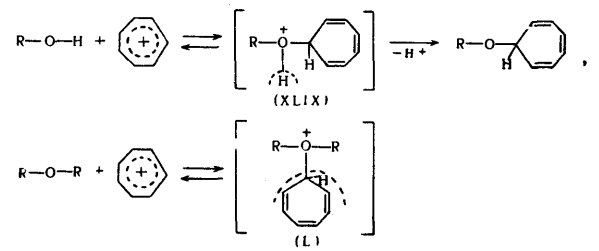
(XLVIII)

where R = R_1 = CH_3 and R = H and R_1 = C_6H_5.

In the study of the interaction of the tropylium ion with ethers the same workers found that bisprimary aliphatic ethers are incapable of interacting with the tropylium ion[160]. Di-isopropyl and dibenzyl ethers do react with the tropylium ion. A hydride ion is then removed directly from the ether molecule. The reaction with di-isopropyl ether yields cycloheptatriene, isopropyl bromide, and acetone and that with dibenzyl ether yields cycloheptatriene, benzyl bromide, and benzaldehyde:

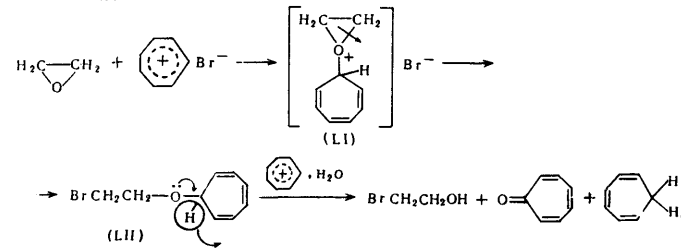


Thus the mechanism of the interaction between the tropylium ion and ether is different from that of its interaction with alcohols. The explanation is probably that in the interaction between alcohols and the tropylium ion hydroxonium compounds (XLIX) are formed, which, on losing a proton, are converted into alkyl tropyl ethers. In their reaction with the tropylium ion ethers can form the oxonium salts (L), which on decomposition most readily split off the tropylium ion, as the most stable carbonium ion, the initial ether being regenerated:



(XLIX) (L)

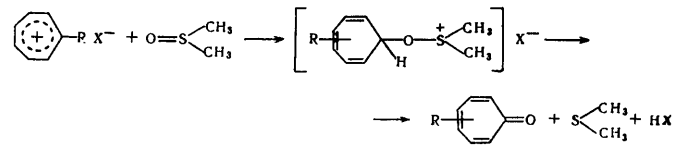
However, the same workers found an example of the reaction[161] in which the ether interacts with the tropylium ion with the intermediate formation of an alkyl tropyl ether. The ether involved in this process is ethylene oxide. The reaction of ethylene oxide with the tropylium ion proceeds as follows:



(LI) (LII)

The C–O bond in the intermediate oxonium compound (LI) readily dissociates as a result of the high strain in the three-membered ring. The β-bromoethyl tropyl ether (LII) was isolated and identified and it was shown that cycloheptatriene, tropone, and ethylene bromohydrin are formed in its reaction with tropylium bromide.

In conclusion one more reaction, which we believe to be of interest, should be mentioned. Kitahara and Funamizu found[162] that tropone is formed in the reaction between the tropylium ion and dimethyl sulphoxide:



1. E. Hückel, Z. Physik, 70, 204 (1931).
2. W. E. Doering and L. H. Knox, J. Amer. Chem. Soc., 76, 3203 (1954).
3. M. E. Vol'pin, Uspekhi Khim., 29, 298 (1960) [Russ. Chem. Rev., 129 (1960)].
4. A. I. Kitaigorodskii, Yu. T. Struchkov, T. L. Khotsynaova, M. E. Vol'pin, and D. N. Kursanov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 39 (1960).
5. M. E. Volpin, D. N. Kursanov, M. M. Shemayakin, V. I. Maimind, and L. A. Neyman, Chem. and Ind., 1261 (1958).
6. W. G. Fateley and E. R. Lippincott, J. Amer. Chem. Soc., 77,

249 (1955).
7. M.E.Vol'pin, K.I.Zhdanova, D.N.Kursanov, V.N.Setkina, and A.I.Shatenshtein, Izv.Akad.Nauk SSSR, Otd.Khim. Nauk, 754 (1959).
8. W.E.Doering and H.Krauch, Angew.Chem., 68, 661 (1956).
9. W.E.Doering and L.H.Knox, J.Amer.Chem.Soc., 79, 352 (1957).
10. Z.N.Parnes, Doctoral Thesis, Institute of Organic-Inorganic ("Organoelemental") Compounds, Moscow, 1965.
11. M.E.Vol'pin, I.S.Akhrem, and D.N.Kursanov, Izv.Akad. Nauk SSSR, Otd.Khim.Nauk, 760 (1957).
12. K.M.Harmon, Diss.Abs., 19, 1563 (1959).
13. N.C.Deno, J.J.Jaruzelski, and A.Schriesheim, J.Amer. Chem.Soc., 77, 3044 (1955).
14. N.C.Deno, N.Friedman, J.D.Hodge, F.P.McKay, and G.Saines, J.Amer.Chem.Soc., 84, 4713 (1962).
15. H.H.Rennhard, E.Heilbronner, and A.Eschenmoser, Chem.and Ind., 415 (1955).
16. G.Naville, H.Strauss, and E.Heilbronner, Helv.Chim. Acta, 43, 1221 (1960).
17. G.Berti, J.Org.Chem., 22, 230 (1957).
18. D.Meuche, H.Strauss, and E.Heilbronner, Helv.Chim. Acta, 41, 57 (1958).
19. M.Stiles and A.J.Libbey, J.Org.Chem., 22, 1243 (1957).
20. A.W.Johnson, A.Langemann, and M.Tišler, J.Chem.Soc., 1622 (1955).
21. K.Conrow, J.Amer.Chem.Soc., 83, 2343 (1961).
22. M.Newman and N.C.Deno, J.Amer.Chem.Soc., 73, 3644 (1961).
23. J.F.J.Dippy, Chem.Rev., 25, 151 (1939).
24. C.Jutz and F.Voithenleitner, Chem.Ber., 97, 29 (1964).
25. M.A.Battiste, J.Amer.Chem.Soc., 83, 4101 (1961).
26. C.Jutz, Angew.Chem., 75, 1119 (1963).
27. C.Jutz and F.Voithenleitner, Chem.Ber., 97, 1337 (1964).
28. C.Jutz and F.Voithenleitner, Chem.Ber., 97, 1590 (1964).
29. C.Jutz, Chem.Ber., 97, 1349 (1964).
30. D.Meuche, H.Strauss, and E.Heilbronner, Helv.Chim. Acta, 41, 414 (1958).
31. D.Sullivan and R.Pettit, Tetrahedron Letters, 401 (1963).
32. Z.N.Parnes, M.E.Volpin, and D.N.Kursanov, Tetrahedron Letters, No.21, 20 (1960).
33. D.N.Kursanov, M.E.Vol'pin, and I.S.Akhrem, Dokl.Akad. Nauk SSSR, 120, 531 (1958).
34. H.McConnel, I.S.Ham, and J.R.Platt, J.Chem.Phys., 21, 66 (1953).
35. L.J.Andrews and R.M.Keefer, "Molecular Complexes in Organic Chemistry" Holden-Day, San Francisco, 1964, pp.19-22.
36. M.Feldman and S.Winstein, J.Amer.Chem.Soc., 83, 3338 (1961).
37. M.E.Vol'pin, I.S.Akhrem, and D.N.Kursanov, Zhur. Obshch.Khim., 28, 330 (1958).
38. H.J.Dauben, F.A.Gadecki, K.M.Harmon. and D.L.Pearson, J.Amer.Chem.Soc., 79, 4557 (1957).
39. K.M.Harmon and A.B.Harmon, J.Amer.Chem.Soc., 83, 865 (1961).
40. K.M.Harmon, A.B.Harmon, and F.E.Cummings, J.Amer. Chem.Soc., 83, 3912 (1961).
41. K.M.Harmon and F.E.Cummings, J.Amer.Chem.Soc., 84, 1751 (1962).
42. K.M.Harmon, A.B.Harmon, and F.E.Cummings, J.Amer. Chem.Soc., 86, 5511 (1964).
43. K.M.Harmon and F.E.Cummings, J.Amer.Chem.Soc., 87, 539 (1965).
44. K.M.Harmon, S.Alderman, K.Benker, D.Diestler, and P.Gebauer, J.Amer.Chem.Soc., 87, 1700 (1965).
45. D.Bryce-Smith and N.A.Perkins, Chem.and Ind., 1022 (1959).
46. D.Bryce-Smith and N.A.Perkins, J.Chem.Soc., 2320 (1961).
47. S.Seto and K.Ogura, Tohoku Daigaku Kagakukeisoku Kenkyusho Hokoku, 9, 111 (1960); Chem.Abs., 55, 24602d (1961).
48. K.M.Harmon, F.E.Cummings, D.A.Davis, and D.J.Diestler, J.Amer.Chem.Soc., 84, 120 (1962).
49. K.M.Harmon, F.E.Cummings, D.A.Davis, and D.J.Diestler, J.Amer.Chem.Soc., 84, 3349 (1962).
50. E.M.Kosower, J.Amer.Chem.Soc., 80, 3253 (1958).
51. E.M.Kosower, J.Org.Chem., 29, 956 (1964).
52. E.Le Goff and R.B.La Caunt, J.Amer.Chem.Soc., 85, 1354 (1963).
53. E.S.Pysh and N.C.Yang, J.Amer.Chem.Soc., 85, 2124 (1963).
54. V.P.Parini, Uspekhi Khim., 31, 822 (1962) [Russ.Chem. Rev., 408 (1962)].
55. A.Streitwieser, Jnr., Tetrahedron Letters, No.6, 23 (1960).
56. M.E.Vol'pin, S.I.Zhdanov, and D.N.Kursanov, Dokl.Akad. Nauk SSSR, 112, 264 (1957).
57. D.H.Geske, J.Amer.Chem.Soc., 81, 4145 (1959).
58. M.E.Vol'pin, Doctoral Thesis, Institute of Organic-Inorganic ("Organoelemental") Compounds, Moscow, 1959.
59. J.dos Santos-Veiga, Mol.Phys., 5, 637 (1962).
60. R.Breslow and H.W.Chang, J.Amer.Chem.Soc., 84, 1434 (1962).
61. R.Breslow and H.W.Chang, J.Amer.Chem.Soc., 87, 2200 (1965).
62. H.J.Dauben and M.R.Rifi, J.Amer.Chem.Soc., 85, 3041 (1963).
63. N.L.Bauld and M.S.Brown, J.Amer.Chem.Soc., 87, 4390 (1965).
64. J.Kwiatek and J.K.Seyler, J.Organometallic Chem., 3, 421 (1965).
65. E.W.Abel, M.A.Bennett, R.Burton, and G.Wilkinson, J.Chem.Soc., 4559 (1958).
66. R.P.M.Werner and S.A.Manastyrskyj, J.Amer.Chem.Soc., 83, 2023 (1961).
67. A.Ledwith and M.Sambhi, Chem.Comm., 64 (1965).
68. C.E.H.Bown, C.Fitzsimmons, and A.Ledwith, Proc.Chem. Soc., 391 (1964).
69. R.Foster and T.J.Thomson, Trans.Faraday Soc., 58, 860 (1962).
70. E.W.Abel, M.A.Bennett, and G.Wilkinson, Proc.Chem. Soc., 152 (1958).
71. H.J.Dauben and L.R.Honnen, J.Amer.Chem.Soc., 80, 5570 (1958).
72. H.J.Dauben and D.J.Bertelli, J.Amer.Chem.Soc., 83, 497 (1961).
73. J.D.Munro and P.L.Pauson, Proc.Chem.Soc., 267 (1959).
74. P.L.Pauson, Proc.Chem.Soc., 297 (1960).
75. J.D.Munro and P.L.Pauson, J.Chem.Soc., 3475 (1961).
76. J.D.Munro and P.L.Pauson, J.Chem.Soc., 3484 (1961).
77. J.D.Munro and P.L.Pauson, J.Chem.Soc., 3479 (1961).
78. M.E.Volpin, D.N.Kursanov, and V.G.Dulova, Tetrahedron, 8, 33 (1960).
79. E.O.Fischer and S.Breitschaft, Angew.Chem., 75, 94 (1963).
80. R.B.King and M.B.Bisnette, Tetrahedron Letters, 1137 (1963).
81. E.O.Fischer and S.Breitschaft, Angew.Chem.Internat. Edn., 2, 100 (1963).
82. R.B.King and F.G.Stone, J.Amer.Chem.Soc., 81, 5263 (1959).
83. G.Allegra and G.Perego, Ricerca sci.Rend., Sez.A, [2], 1, 362 (1961); Chem.Abs., 62, 4742d (1965).
84. H.P.Fritz and C.G.Kreiter, Chem.Ber., 97, 1398 (1964).
85. E.O.Fischer and H.P.Fritz, Z.phys.Chem.(Frankfurt), 17,

132 (1958).
86. J.E.Mahler, D.A.I.Jones, and R.Pettit, J.Amer.Chem. Soc., 86, 3589 (1964).
87. J.L.Rosenberg, J E.Mahler, and R.Pettit, J.Amer.Chem. Soc., 84, 2842 (1962).
88. S.Winstein, H.D.Kaecz, C.G.Keiter, and E.C.Friedrich, J.Amer.Chem.Soc., 87, 3267 (1965).
89. G.N.Schrauzer, J.Amer.Chem.Soc., 83, 2966 (1961).
90. A.Davison, W.McFarlane, L.Pratt, and G.Wilkinson, J.Chem.Soc., 4821 (1962).
91. J.P.Dahl and C.J.Ballhausen, Kgl.danske Videnskab.Selskab, Mat.-fys.Medd., 33, 22 (1961); Chem.Abs., 61, 1379g (1964).
92. E.M.Shustorovich and M.E.Dyatkina, Dokl.Akad.Nauk SSSR, 128, 1234 (1959).
93. A.W.Johnson and M.Tîšler, Chem.and Ind., 1427 (1954).
94. M.J.S.Dewar and C.R.Ganellin, J.Chem.Soc., 2438 (1959).
95. M.A.Battiste, J.Amer.Chem.Soc., 85, 2175 (1963).
96. M.J.S.Dewar and R.Pettit, J.Chem.Soc., 2021 (1956).
97. M.J.S.Dewar and R.Pettit, Chem.and Ind., 199 (1955).
98. D.N.Kursanov and M.E.Vol'pin, Dokl.Akad.Nauk SSSR, 113, 339 (1957).
99. C.Jutz, Chem.Ber., 97, 2050 (1964).
100. T.Nozoe and K.Takahashi, Bull.Chem.Soc.Japan, 38, 665 (1965).
101. M.E.Vol'pin and I.S.Akhrem, Dokl.Akad.Nauk SSSR, 161, 597 (1965).
102. E.Weth and A.S.Dreiding, Proc.Chem.Soc., 59 (1964).
103. G.A.Gladkovskii, S.S.Skorokhodov, S.G.Slyvina, and A.S.Khachaturov, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 1273 (1963).
104. D.J.Bertelli, C.Golino, and D.L.Dreyer, J.Amer.Chem. Soc., 86, 3329 (1964).
105. J.W.Wilt and D.Piszkiewicz, Chem.and Ind., 1761 (1963).
106. A.G.Anderson and L.L.Reploge, J.Org.Chem., 28, 262 (1963).
107. R.W.Murray and M.L.Kaplan, Tetrahedron Letters, 2903 (1965).
108. A.N.Nesmeyanov and R.V.Golovnya, Dokl.Akad.Nauk SSSR, 133, 1337 (1960).
109. A.N.Nesmeyanov and R.V.Golovnya, Zhur.Obshch.Khim., 31, 1067 (1961).
110. D.H.Reid, M.Frazer, B.B.Molloy, H.A.S.Paym, and R.G.Sutherland, Tetrahedron Letters, 530 (1961).
111. H.Volz and M.J.Volz, Tetrahedron Letters, 1871 (1964).
112. H.Volz, Tetrahedron Letters, 1965 (1963).
113. H.Volz, Angew.Chem., 75, 921 (1963).
114. H.Volz, Tetrahedron Letters, 1899 (1964).
115. H.Volz and M.J.Volz, Tetrahedron Letters, 3413 (1965).
116. R.van Helden, A.P.ter Borg, and A.F.Bickel, Rec.Trav. chim., 81, 599 (1962).
117. K.Hafner, A.Stephan, and C.Bernhard, Annalen, 650, 42 (1961).
118. A.P.ter Borg, R.van Helden, and A.F.Bickel, Rec.Trav. chim., 81, 164 (1962).
119. A.P.ter Borg, R.van Helden, and A.F.Bickel, U.S.P. 3110735 (1963); Chem.Abs., 60, 2866 (1964).
120. T.Nozoe, Jap.P. 17674 (1964); Chem.Abs., 62, 5234a (1965).
121. M.J.S.Dewar, C.R.Ganellin, and R.Pettit, J.Chem.Soc., 55 (1958).
122. G.Juppé and A.P.Wolf, Chem.Ber., 94, 2328 (1961).
123. T.Nozoe, T.Mukai, T.Tezuka, and K.Osaka, J.Chem.Soc. Japan, 84, 662 (1963).
124. K.Conrow, J.Amer.Chem.Soc., 81, 5461 (1959).
125. M.E.Vol'pin, I.S.Akhrem, and D.N.Kursanov, Zhur. Obshch.Khim., 30, 1187 (1960).
126. T.Mukai and H.Tsuruta, Bull.Chem.Soc.Japan, 37, 1018 (1964).
127. T.Mukai and T.Miyashi, Bull.Chem.Soc.Japan, 38, 469 (1965).
128. T.Nozoe, T.Tezuka, and T.Mukai, Bull.Chem.Soc.Japan, 36, 1470 (1963).
129. C.Rüchardt and H.Schwarzer, Angew.Chem., 74, 251 (1962).
130. J.Degani and R.Fochi, Boll.sci.Fac.Chim.ind.Bologna, 20, 139 (1962); Chem.Abs., 59, 3829h (1963).
131. J.Degani and R.Fochi, Boll.sci.Fac.Chim.ind.Bologna, 20, 141 (1962); Chem.Abs., 59, 3829h (1963).
132. W.E.Doering and L.E.Helden, J.Chem.Soc., 482 (1961).
133. J.J.Looker, J.Org.Chem., 30, 638 (1965).
134. P.N.Rylander, S.Meyerson, and H.M.Grubb, J.Amer. Chem.Soc., 79, 842 (1957).
135. S.Meyerson, P.N.Rylander, E.L.Eliel, and J.D.McCollum, J.Amer.Chem.Soc., 81, 2606 (1959).
136. S.Meyerson, J.D.McCollum, and P.N.Rylander, J.Amer. Chem.Soc., 83, 1401 (1961).
137. S.Meyerson, J.Amer.Chem.Soc., 85, 3340 (1963).
138. V.Hanuš and Z.Doleyšek, Coll.Czech.Chem.Comm., 28, 652 (1963).
139. C.Lifschitz and S.H.Bauer, J.Phys.Chem., 67, 1629 (1963).
140. B.Föhlisch, P.Burgle, and D.Krokenberger, Angew. Chem., 77, 1019 (1965).
141. K.Hafner, H.W.Riedel, and M.Danielicz, Angew.Chem., 75, 344 (1963).
142. M.E.Vol'pin, I.S.Akhrem, and D.N.Kursanov, Izv.Akad. Nauk SSSR, Otd.Khim.Nauk, 1501 (1957).
143. N.W.Jordan and J.W.Elliott, J.Org.Chem., 27, 1445 (1962).
144. T.Nozoe, S.Itô, and T.Tezuka, Chem.and Ind., 1088 (1960).
145. Y.Kitahara, I.Murata, and T.Asano, Bull.Chem.Soc. Japan, 37, 924 (1965).
146. M.E.Vol'pin, I.S.Akhrem, and D.N.Kursanov, Dokl. Akad.Nauk SSSR, 120, 531 (1958).
147. R.W.Hoffmann, Angew.Chem., Internat.Edn., 4, 977 (1965).
148. A.E.Borisov, A.N.Abramova, and Z.N.Parnes, Izv.Akad. Nauk SSSR, Otd.Khim.Nauk, 943 (1964).
149. N.Kornblum and G.D.Cooper, J.Amer.Chem.Soc., 72, 3013 (1950).
150. A.I.Brodskii and L.V.Sulima, Dokl.Akad.Nauk SSSR, 85, 1277 (1952).
151. Z.N.Parnes, G.D.Mur, R.V.Kudryavtsev, and D.N.Kursanov, Dokl.Akad.Nauk SSSR, 155, 1371 (1964).
152. P.D.Bartlett and J.D.McCollum, J.Amer.Chem.Soc., 78, 1441 (1956).
153. S.G.Entelis, G.V.Èpple, and N.M.Chirkov, Dokl.Akad. Nauk SSSR, 136, 667 (1961).
154. S.G.Entelis, R.P.Tiger, G.V.Epple, and N.M.Chirkov, Dokl.Akad.Nauk SSSR, 137, 1420 (1961).
155. S.G.Entelis and G.V.Epple, Dokl.Akad.Nauk SSSR, 141, 121 (1961).
156. G.V.Epple, V.P.Odintsova, and S.G.Entelis, Kinetika i Kataliz, 2, 821 (1961).
157. A.P.ter Borg, R.van Helden, A.F.Bickel, W.Renold, and A.S.Dreiding, Helv.Chim.Acta, 43, 457 (1960).
158. T.Ikemi, T.Nozoe, and H.Sugiyama, Chem.and Ind., 932 (1960).
159. M.E.Vol'pin, Z.N.Parnes, and D.N.Kursanov, Izv.Akad. Nauk SSSR, Otd.Khim.Nauk, 950 (1960).
160. D.N.Kursanov, Z.N.Parnes, and G.D.Kolomnikova, Zhur. Org.Khim., 3, 1060 (1967).
161. Z.N.Parnes, G.D.Mur, and D.N.Kursanov, Dokl.Akad. Nauk SSSR, 159, 857 (1964).

162. Y. Kitahara and M. Funamizu, Jap. P. 11 122 (1962); Chem. Abs,, 59, 100 126 (1963).

Institute of Organic-Inorganic
("Organoelemental") Compounds,
USSR Academy of Sciences,
Moscow

U. D. C. 547.751 : 747.753

SYNTHESIS OF SUBSTITUTED INDOLES VIA INDOLINES

M. N. Preobrazhenskaya

CONTENTS

I. Introduction 753

II. Methods of preparation of indolines 754

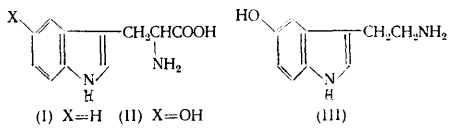
III. Introduction of substituents into the benzene ring of the indoline molecule 758

IV. Introduction of substituents into the pyrrole ring of the indoline molecule 763

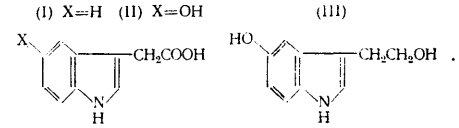
V. Conversion of indoline derivatives into indoles 764

I. INTRODUCTION

Indole derivatives play an important role in vital processes [1,2]. Of special importance are the essential amino-acid tryptophan (I) and the products of its metabolism, for example, 5-hydroxytryptophan (II), serotonin (III), 3-indolylacetic (IV) and 5-hydroxy-3-indolylacetic (V) acids, 5-hydroxytryptophol (VI) and a number of other substances:

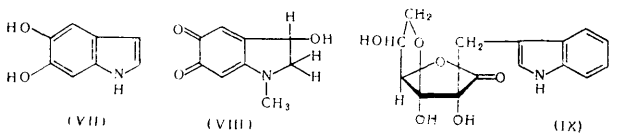


(I) X=H (II) X=OH (III)



(IV) X=H (V) X=OH (VI)

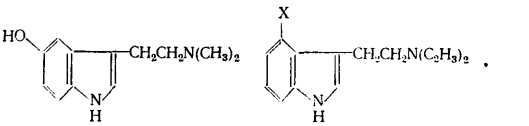
The structure of 5,6-dihydroxyindole (VII) is the basis of the animal pigment melanin [3]. The processes involved in the biosynthesis of melanin are closely related to the metabolism of aminocatechols, including adrenalin and tyrosine. One of the products of adrenalin metabolism is adrenochrome (VIII) [4]. It has been shown recently [5] that ascorbic acid in plants exists in a bound form as two diastereoisomeric ascorbigens A and B (IX):



(VII) (VIII) (IX)

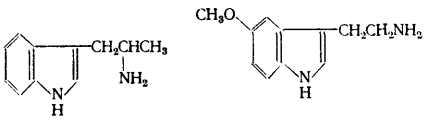
ascorbigen B

Many compounds containing the indole ring exhibit high pharmacological activity. It is sufficient to recall reserpine and other Rauwolfia alkaloids, lysergic acid, brucine, yohimbine, eserine, and other alkaloids, and also halucinogenic compounds such as bufotenin (X) (a component of frog venom), psilocin (XI), psilocybin (XII), and others [1].



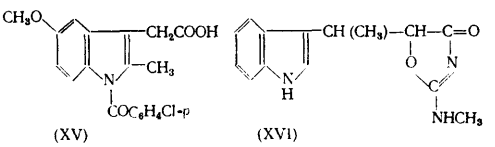
(X) (XI) X=OH (XII) X=OPO_3H_2

The synthetic research on pharmacologically active compounds in the indole series has proved extremely fruitful. In particular, valuable medicinal substances have been found—indopane [6] (3-indolylisopropylamine) (XIII), used as a stimulating antidepressant in psychiatry and mexamine (5-methoxytryptamine) (XIV) [7], used in the prophylaxis of radiation damage:



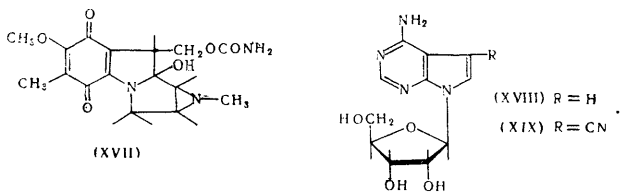
(XIII) (XIV)

Considerable interest was aroused by the discovery of indole derivatives with high anti-inflammatory activity, among which the most important is indomethacin—1-(*p*-chlorobenzoyl)-5-methoxy-2-methylindole-3-acetic acid (XV) [8]:



(XV) (XVI)

Until recently indole derivatives with high antimicrobial activity were unknown. However, the first communication dealing with the antibiotic indolmycin (XVI), which inhibits the development of strains of *Staphylococcus aureus*, a micro-organism resistant to the most widely used antibiotics, appeared in 1961. [9,10] Vigorous studies are being made on the synthesis of the antibiotic mitomycin (XVII) and related compounds which exhibit high cytostatic, bacteriostatic, and fungicidal activity [11,12]:



(XVII) (XVIII) R = H (XIX) R = CN

The reports of the discovery of a new group of antibiotics, tubercidin (XVIII) and toyokamycin (XIX) [13], are extremely interesting. These compounds are based on the 5,7-diazaindole (pyrimidinopyrrole) structure.

The structure of many indole compounds is based on tryptophan, indole-3-acetic acid, or tryptamine (3-indolylethylamine). In this connection methods of synthesising the side-chain in position 3 of the indole ring have been developed in special detail. The method of introducing substituents in position 1 have been investigated much less,