Tetrahedron Vol. 43, No 17, pp. 3839-3861, 1987
Printed in Great Britain.

0040-4020/87 $5.00+.00
Pergamon Journals Ltd.

TETRAHEDRON REPORT NUMBER 224

ETHYLENIC COMPOUNDS AS PROBES FOR THE STUDY OF DONOR-ACCEPTOR INTERACTION

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(*Received* 31 *March* 1987)

CONTENTS

Abstract—The ethene bond is sensitive to a change in electron density which causes its opening or rotation. This makes it possible to use ethene compounds as probes for studying the mechanism of the reactions accompanied with generation of particles of a radical nature or with charge (electron) transfer. It also becomes possible to control transformations peculiar to ethene compounds including isomerization, saturation, and cyclodimerization.

1. INTRODUCTION

In recent years chemistry has been enriched with a wide set of instrumental investigations. This has prompted studies of many intermediate particles whose formation is a necessary condition for transformation of an initial compound into a final one. As a result, new methods of achieving chemical reactions have been developed which allow one to prepare the desired products in higher yields, at higher rates, and with higher selectivity. New particles previously unknown in chemistry were revealed and studied, in particular, ion-radicals and electron donor–acceptor complexes. It was also shown that donor–acceptor interaction giving rise to complexes and ion-radicals is a necessary intermediate stage of many reactions in organic and organometallic chemistry. At the same time it became urgent to develop methods of revealing donor–acceptor interactions, both instrumental and chemical. Chemical methods are especially valuable since a chemist–experimenter can obtain the required evidence just in the laboratory.

This report deals with one of chemical methods, namely, probing with the aid of ethene compounds. It will be shown that the method detects donor–acceptor stages of the process with a high degree of reliability and is rather simple. The relevant literature data are summarized for the first time.

2. PROBING WITH THE AID OF VINYL TYPE MONOMERS

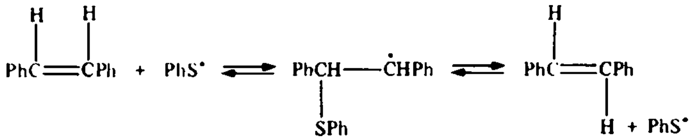
Donor–acceptor interactions may involve "weak", "medium strength", and "strong" complexes with charge transfer, ion-radical pairs, and, finally, free ion-radicals. Scheme 1 illustrates these stages in the interaction of donor D with acceptor A: the complexation stage is given in a general form without taking into account the charge transfer degree. In those (rather frequent) cases where the transfer of a complete charge (electron) takes place, ion-radicals or radicals arise which can be revealed. This problem cannot always be solved easily even when the most modern physical methods are used.

$$D + A \longrightarrow D^{\delta+}; A^{\delta-} \longrightarrow D^{+\bullet}; A^{-\bullet} \longrightarrow D^{+\bullet} + A^{-\bullet}$$

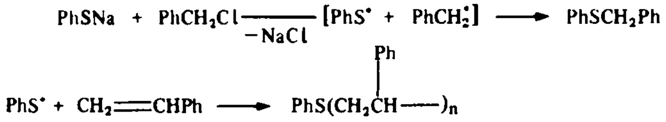
Scheme 1.

Consider by way of an example reaction (2) related to the formation of unstable phenylthiyl radicals upon one-electron oxidation of the phenylthiolate ion.[1]

To reveal the PhS˙ radical, use was made[2] of its propensity to add reversibly to stilbene, thereby causing *cis–trans*-isomerization of stilbene (Scheme 2). It should be noted (since it is important for further presentation) that the reversibility of reaction (2) concerns only the addition–detachment of the phenylthiyl radical. *trans*-Stilbene is more stable than its *cis*-isomer, the difference in energies being[3] about 45 kJ mol^{-1}. Therefore in reaction (2) only *cis* → *trans* but not *trans* → *cis* isomerization takes place. It is also noteworthy that the ethene bond in stilbene is protected by phenyl groups which are known to hinder further polymerization. The removal of phenyl shielding even from one side of the ethene fragment makes polymerization possible. This provides a new way to identify the radical generation mechanism using styrene polymerization. For instance, it was shown that in reaction of sodium thiophenolate with alkyl halides, 2-butyltosylate,[4] or benzyl halides,[5] electron transfer takes place with the formation of the phenylthiyl radical. The radical can be captured if styrene is introduced into the system. Even small amounts of the phenylthiyl radical induce styrene polymerization and the PhS fragment is inserted into the polymer. When the thiophenolate is mixed with styrene in the absence of the acceptor component (i.e. without alkyl halide or tosylate), the polymer is not formed. The introduction of a radical trap (phenyl-*t*-butylnitroxide) into the reaction mixture slows down the transformation of the acceptor component and the product of addition of the phenylthiyl radical to the nitroxide was detected by the ESR method. All this points to the formation of phenylthiyl radicals on the main pathway of the reaction (Scheme 3).

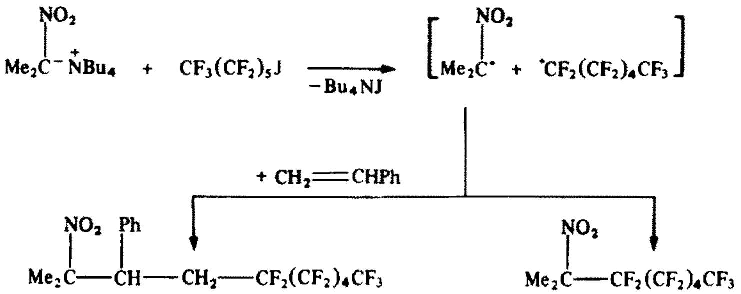


Scheme 2.



Scheme 3.

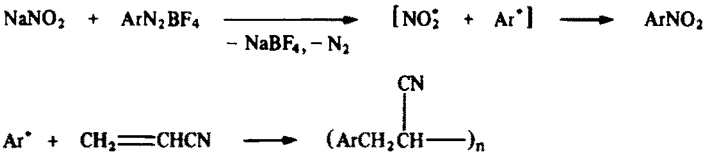
The presence in the reaction mixture of another radical (benzyl) does not hinder the propagation of a polymer chain. This radical belongs to the π-type, that is it is more stable than the radical adduct formed after the addition of PhS˙ to styrene. In the same manner a radical including two or more styrene fragments reacts with styrene faster than the benzyl radical. Thus, polymerization is a result of great difference in the stabilities of primary radicals formed after donor–acceptor interaction of the reagent and substrate. If such interaction yields radicals of identical activities, the presence of a styrene gives rise not to a polymer but to a low-molecular individual compound containing fragments of the probe and of both radicals formed. This point can be exemplified by the reaction of perfluoroalkyl iodide (substrate) with a nitropropenide salt (reagent) in the presence of a monomer probe (vinyl acetate, methylmethacrylate, styrene)[6] (Scheme 4).



Scheme 4.

The polymerization of a vinyl compound or the formation of a low-molecular addition product is a simple and clear proof of the ion-radical reaction route. However, a warning should be made: that the probe method, just as any other method, is not free from artefacts.

For instance, it was shown with the aid of the acrylonitrile probe[7] that the replacement of the diazo group with the nitro group in aryldiazonium fluoroborates gives aryl radicals under the action of sodium nitrite. The addition of acrylonitrile to the reaction mixture gives rise to a polymer. The polymerization proceeds only in nitrogen whereas oxygen inhibits it. Benzene-, *p*-nitrobenzene-, and *p*-methoxybenzenediazonium fluoroborates were used as substrates. With all these substrates the acrylonitrile test was positive. The final nitro compound, however, (Scheme 5) was formed only from the first two substrates. Methoxybenzenediazonium salts did not give nitroanisole because the *p*-methoxyphenyl radical did not couple with the nitrite radical. These facts are taken into account in Scheme 5.



$$NaNO_2 + ArN_2BF_4 \xrightarrow[-NaBF_4,\,-N_2]{} [NO_2^{\bullet} + Ar^{\bullet}] \longrightarrow ArNO_2$$

$$Ar^{\bullet} + CH_2{=}CHCN \longrightarrow (ArCH_2\overset{CN}{\overset{|}{C}H}{-})_n$$

Scheme 5.

Of fundamental importance is the use of a vinyl monomer as a reaction medium in kinetic investigations. In essence, the monomer acts again as a probe so the reaction rates are compared in, for instance, styrene and benzene. If the reaction proceeds via the formation of radicals, the probabilities of radical emergence from the cage into the bulk of the solution are different. Styrene as a solvent favours the emergence into the bulk since the radicals have a greater affinity for styrene than for benzene. On the basis of the above approach the cryptoradical mechanism of oxidation of phosphines with hydroperoxides was proved[8,9] (Scheme 6). The oxidation constant, k_{ox}, is found by

$$(R^1O)_3P + R^2OOH \xrightarrow[-R^2OH]{} (R^1O)_3PO$$

Scheme 6.

determining polarographically the rate of hydroperoxide consumption. The action of phosphines as polymer stabilizers, which inhibit the adverse effect of hydroperoxides formed in polymers in air, is based on reaction (6). Studies of the mechanism of the stabilizing effect are, undoubtedly, of great importance. It was shown[8] that reaction (6) proceeds via the stage of electron transfer with subsequent formation of radicals (Scheme 7). The radicals then react without emergence into the bulk and cannot be detected by the ESR method. It becomes necessary to introduce an external compound (iminoxyl radical) and to follow the decrease in its concentration due to the reaction with the intermediate particles formed following Scheme 7. In this manner the consumption constant k_{cons} for the iminoxyl radical is determined. In full agreement with the initial prerequisites it was found[8,9] that $k_{ox}^{bnz} \simeq k_{cons}^{bnz} < k_{cons}^{styr}$.

$$(R^1O)_3P + R^2OOH \longrightarrow [(R^1O)_3P^{+\bullet} + R^2OOH^{-\bullet}] \longrightarrow$$

$$\longrightarrow [(R^1O)_3\dot{P}OH + R_2O^{\bullet}] \longrightarrow R_2OH + (R^1O)_3PO$$

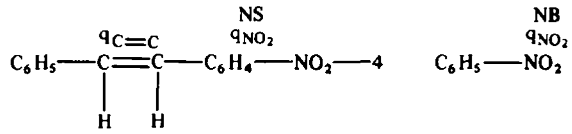
Scheme 7.

3. ROTATION ABOUT THE ETHYLENE BOND AS A CRITERION OF DONOR-ACCEPTOR INTERACTION

Vinyl monomers considered in the previous section act as interceptors of radicals which are the secondary products of donor–acceptor interaction. However, it is possible to use ethene probes at earlier stages to examine the formation of electron donor–acceptor complexes or ion-radicals. In this case ethene compounds are involved in complexation or electron exchange with the donor or the acceptor and their geometry changes. The change in the geometry is a result of rotation about the ethylene bond and may take place in the course of the addition or depletion of one electron. The forms with negative and positive charges will be considered individually.

3.1. *Ethylenes enriched with negative electron density*

Compare the anion-radicals of nitrobenzene and 4-nitrostilbene. They seem to be similar with respect to the distribution of the transferred electron so an opinion[10] was expressed that in aromatic nitro derivates the lowest unoccupied orbital (in which an unpaired electron is localized) is, in fact, an orbital of the nitro group. However, a comparison of *cis*-4-nitrostilbene and nitrobenzene in anion-radical states by a quantum chemical MO LCAO method in a CNDO/2 approximation gave another picture.[11] In the 4-nitrostilbene anion-radical an unpaired electron should be predominantly localized not at the nitro group but at the ethylene bond. This results from comparing the q values which characterize the population of the fragments with one electron located in the lowest unoccupied orbital (Scheme 8).



NS NB

$q_{NO_2} = 0.0764$, $q_{NO_2} = 0.3852$, $q_{C=C} = 0.2629$

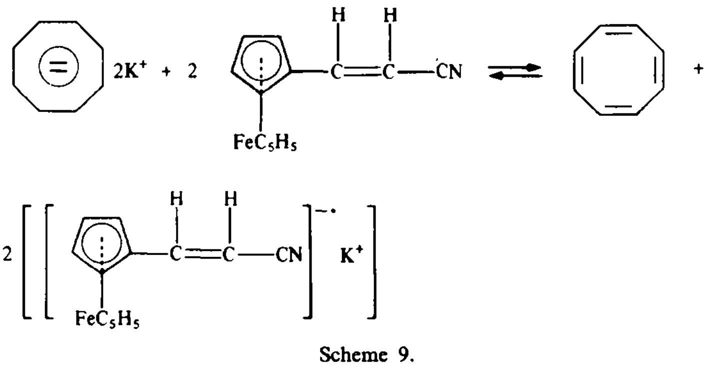
Scheme 8.

Thus, it follows from this theoretical data for anion-radicals that the introduction of a styryl substituent at position 4 in nitrobenzene should cause a shift of spin density to the olefin bond. This is why the transformation into the *trans*-form is observed in the case of the *cis*-4-nitrostilbene anion-radical.[12] For unsubstituted *cis*-stilbene (neutral molecule), calculations by the MO LCAO method in the Coulson–Haye approximation give[3] the value of the *cis–trans* isomerization barrier equal to 150 kJ mol^{-1}, whereas for the anion-radical this value is 70 kJ mol^{-1}. The rotation barrier of *cis*-stilbene decreases almost by half when passing from neutral *cis*-stilbene to the anion-radical. But this does not allow one to draw an automatic conclusion in any olefin that the rotation barrier is reduced when an additional electron is captured. For instance, a 4,4′-dinitrostilbene anion-radical undergoes complete *cis–trans* isomerization[13] whereas the *cis*-2,4-dinitrostilbene anion-radical retains its geometry.[14] The ability to isomerize is determined not only by electron capture but also by the delocalization of the electron in the system of bonds in the anion-radical. A quantum-chemical index, $J = \int \pi_g \psi_f d\tau$, has been proposed[15] which characterizes the tendency of anion-radicals of the stilbene series to *cis–trans* isomerization. The index represents the overlapping integral of the π_g

orbital of a *cis* anion-radical (which is completely localized at the ethylene bond) with the ψ_f molecular orbital occupied by one electron. If $J = 1$, antibonding in the olefin bond in the anion-radical should be at its maximum, i.e. *cis* → *trans* conversion proceeds readily. If $J = 0$, no antibonding in the olefin bond is observed and rotation about it remains forbidden. The difference between *cis* anion-radicals of 4,4′- and 2,4-dinitrostilbenes described above correlates perfectly with that between the indices J which are equal to 0.45 and 0.01, respectively.

Anion-radicals of indigoids as well as the anion-radical of 4,4′-dinitrosilbene are characterized by the location of spin density within the limits of the exocyclic double bond.[16] If a mixture of *cis* and *trans* isomers of thioindigo is treated with a small amount of potassium with dimethoxyethane as a solvent, a complete stereomutation of *cis*-thioindigo into its *trans* isomer is observed.[17] Obviously, some of the thioindigo molecules are reduced in the system and then exchange electrons with the remaining neutral molecules. Thus, for some time all *cis* isomer molecules are in the form carrying excess electron density. This time is sufficient for *cis* → *trans* conversion to take place.

Not only metals but also organic compounds with rather low ionization potentials may act as electron donors. The cyclooctatetraene dianion whose dipotassium salt is soluble in ethers is a convenient alternative to alkali metals. This makes it possible to use the dianion as a "dissolved electrode" and to evaluate the extent of electron transfer by measuring the extent of formation of neutral cyclooctatetraene[18] (Scheme 9). Scheme 9 shows α-ferrocenyl-β-cyanoethylene as an acceptor: the reaction is reversible and the presence of all four components in the reaction mixture has been proved. The character of equilibrium 9 is such that the extent of electron transfer is only 20%.[19] A calculation of the equilibrium constant with due regard for redox potentials of the donor and the acceptor gives[20] the same value of the yield of the reaction 9 products. Primary anion-radicals of *cis* α-ferrocenyl-β-cyanoethylene isomerize into the *trans*-form with a conversion of 65%. No other changes (dimerization, double bond saturation, or cleavage) occur with the ferrocenyl substrate. The *trans*-isomer used as an acceptor transforms into the anion-radical in a similar yield without any change in geometry. One may conclude that the energy level of the anion-radical formed from *trans*-ferrocenylcyanoethylene lies considerably lower than the energy level of the anion-radical from *cis*-ferrocenylcyanoethylene (only *cis* → *trans* rather than *trans* → *cis* isomerization is observed). Furthermore the formation of anion-radicals of the substrate not only follows Scheme 9 but also involves electron exchange between these anion-radicals and uncharged ferrocenylcyanoethylene molecules which are also present in the solution [the *cis* → *trans* isomerization degree exceeds more than three times the extent of electron transfer from the cyclooctatetraene dianion by reaction (9)]. Thus, the possibility suggested in the case with thioindigo was directly proved for ferrocenylcyanoethylene. Electron exchange may increase considerably the equilibrium concentration of anion-radicals and enhance the extent of *cis* → *trans* isomerization.



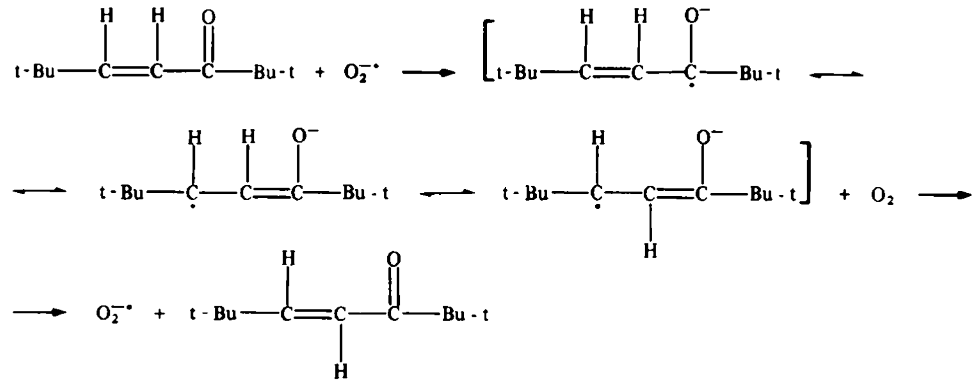
Scheme 9.

An electron exchange between the anion-radical and the initial neutral molecule is a fast process. It ends before the anion-radical becomes involved in further transformations. For instance, nucleophilic addition of a lithium cuprate to an α,β-unsaturated ketone gives a saturated ketone with an extra alkyl group[21,22] (Scheme 10). When an excess of the ketone is used, *cis* → *trans* isomerization is observed in the portion of the ketone where no addition to the ethylene bond has occurred. The authors believe that isomerization points to a two-stage rather than direct addition of the lithium cuprate to the ethylene bond. The process includes primary formation of the anion-radical of the

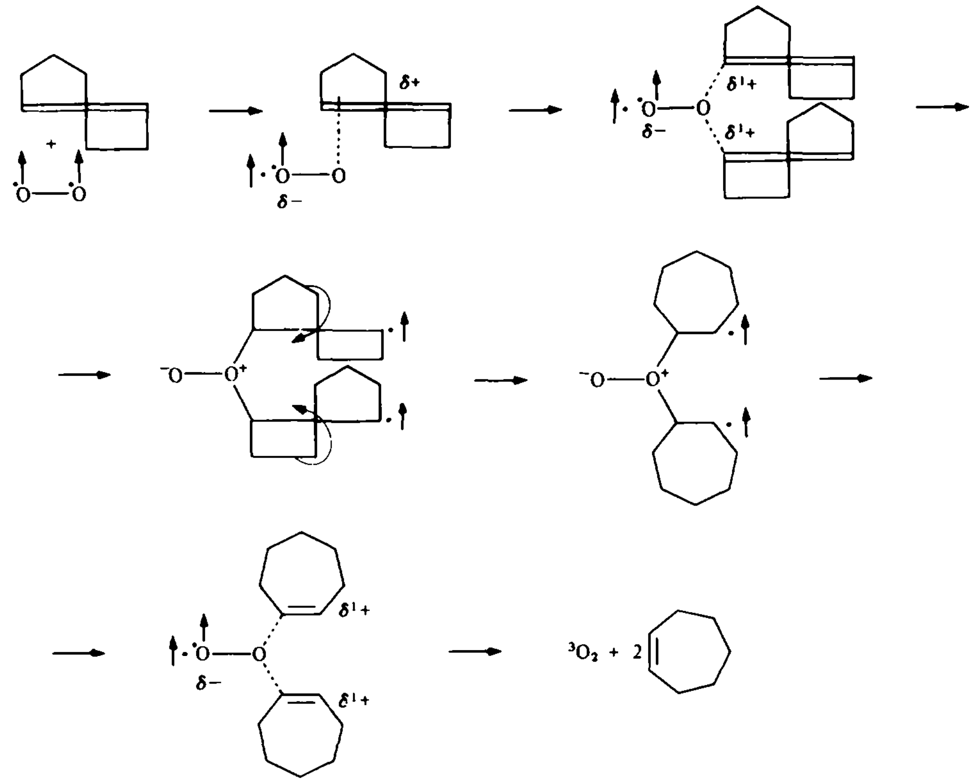
α,β-unsaturated ketone. This anion-radical is then involved in two reactions, namely, addition and electron exchange. It is the exchange which causes isomerization of the excess of the unsaturated ketone.


Scheme 10.

The ketone shown in Scheme 10 was used to reveal the ability of a peroxide radical anion, generated from potassium peroxide in benzene under the action of 18-crown-6-ether, to electron transfer.[23] The peroxide radical anion gives oxygen after electron transfer to the ketone. The oxygen then oxidizes the intermediate radical anion which immediately yields the *trans* form of the α,β-unsaturated ketone (Scheme 11). It should be noted, however, that in the course of reaction (11) oxygen is formed at an intermediate stage. Oxygen itself can induce *Z*/*E* isomerization of ethene compounds and produce electron donor–acceptor complexes. Thermal *trans* → *cis* isomerization of cycloheptene catalyzed by oxygen illustrates this point[24] (Scheme 12). The ethylene bond in *trans*-cycloheptene is strained whereas in the *cis* form such strain is reduced. The stress energy of *trans*-cycloheptene is about 110 kJ mol^{-1}. In spite of this fact, *trans*-cycloheptene is quite stable at $-78°C$ but upon heating it is transformed quantitatively into the *cis* isomer. The isomerization mechanisms are different in nitrogen and in air. In nitrogen the process obeys first order dependence whereas in air thermal isomerization has second order. The activation energy and the isomerization frequency factor are more favourable in air than in nitrogen. A strongly negative value of the activation entropy should especially be noted: this value can be a result of molecular association which takes place in the presence of oxygen according to Scheme 12 and facilitates *trans* → *cis* conversion. It is assumed[24] that the reaction is initiated by a collision complex in which the collision of *trans*-cycloheptene with triplet oxygen, which is in excess, is most effective. The excessive oxygen molecules do not participate in isomerization (the use of oxygen instead of air does not have any noticeable effect). The collision complex transforms into a donor–acceptor complex of a 2:1 composition without triplet–singlet transformation of oxygen. Then a zwitter–ion intermediate state arises with the formation of real C–O bonds and spontaneous *trans–cis* isomerization occurs. In this way a donor–acceptor complex of triplet oxygen with *cis*-cycloheptene is produced which is less stable than a similar complex with *trans*-cycloheptene. The complex formed dissociates immediately, recovering triplet oxygen and yielding free *cis*-cyclohexene. These transformations are shown in Scheme 12.

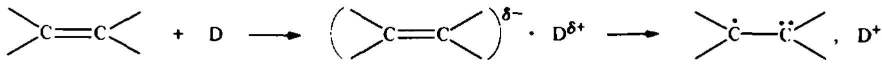

Scheme 11.

Scheme 12 includes the formation of a rather specific donor–acceptor complex. It would be interesting and important to know that in ordinary electron donor–acceptor complexes isomerization of ethene components may also take place. According to Mulliken's concepts adopted in organic chemistry, such complexes contain an acceptor (A) enriched with a proportion of electron density,



Scheme 12.

and a donor (D) depleted of an electron in the same proportion (Scheme 13). The Scheme also demonstrates that complexes and ion-radicals have a genetic relationship.



Scheme 13.

At present new ideas arise concerning the nature of these complexes (see, for instance[25]). We are interested in the behaviour of ethene compounds in the anion-radical state and in complexes with donors. This problem was studied[11] in an example of dimethylaniline complexes with nitrobenzene and *cis*-4-nitrostilbene (cyclohexane was used as a solvent). The spectroscopic properties of the complexes, their composition, (1 : 1) and their formation constants, k_{form}, were determined (Table 1). The formation constant for nitrostilbene is almost 4 times greater than that of nitrobenzene but the composition of the complexes was identical. There is another essential difference between

Table 1. Characteristics of electron acceptors: nitrobenzene (NB) and *cis*-4-nitrostilbene (NS)

Acceptor		Complex with DMA[a]	
Symbol	E_{LUMO} (kJ mol^{-1})[b]	Composition	k_{form} (l mol^{-1})
NB	135	1 : 1	0.08
NS	39	1 : 1	0.29[c]

[a] DMA = N,N-dimethylaniline.

[b] Calculation by the MO LCAO SCF method in the CNDO/2 approximation.

[c] Bonding into a complex is accompanied by *cis* → *trans* conversion (Table 2).

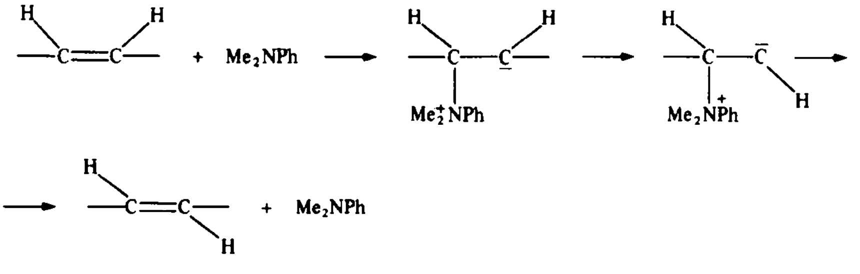
Table 2. *Trans* conversion (C) of *cis*-nitrostilbenes induced by dimethylaniline (donor/acceptor ratio 1 : 1, 25°C, 24 h without solvent, followed by dilution with acetone)

Acceptor (*cis* form)	J for anion-radical[a]	C (%)[b]
2,4-Dinitrostilbene	0.01	0
2-Nitrostilbene	0.31	42
4-Nitrostilbene	0.45	63
α,β-Dinitrostilbene	0.61	99

[a] $J = \int \pi_g \psi_f d\tau$ (see in the text).

[b] Average of 3–5 experimental runs.

these two complexes. Dilution with cyclohexane causes decomposition of the complexes into their components: nitrobenzene is released unchanged but *cis*-4-nitrostilbene appears as the *trans*-isomer. The k_{form} values agree with the differences in LUMO energies (E_{LUMO}, Table 1) for the acceptors under study and the observed *cis* → *trans* conversion agrees with the difference in spin density distribution between the corresponding anion-radicals (Scheme 7). No anion-radicals were detected on interaction with dimethylaniline. The calculation of the equilibrium constant of a one-electron transfer on the basis of corresponding redox-potentials shows that this process is hardly probable. For instance, interaction of dimethylaniline with *cis*-4-nitrostilbene is characterized by the equilibrium constant, 6.6×10^{-27}. At the same time it was noted[15] that the conversion degree of different nitrostilbenes under the action of dimethylaniline changes in the same manner as index J for the same nitrostilbenes in an anion-radical state (Table 2). Since the formation of anion-radicals as a result of electron transfer from dimethylaniline to nitrostilbenes is not probable, the correlation with the J value may be due to a charge transfer from the donor to the acceptor. This transfer involves the lowest free orbital which is populated by a single electron (the transfer of a total charge) in the anion-radical. The formation of a donor–acceptor complex may favour not the *cis* → *trans* isomerization itself but either the addition of an amine to the olefinic bond (Scheme 14) or deprotonation by the amine according to Scheme 15. In this case isomerization is also possible but donor–acceptor interaction is not a direct cause of it.



Scheme 14.

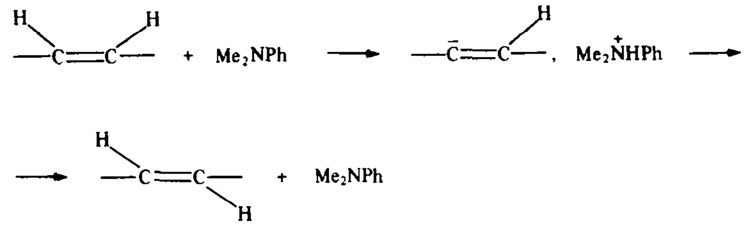
In paper[26] mechanisms 14 and 15 were rejected for the following reasons:

(1) Dimethylamine is not prone to the addition in Scheme 14 because of a strong shielding of the amino group.

(2) If it is still assumed that such an addition does take place 2,4-dinitrostilbene should undergo conversion as 2-nitrostilbene does. The observed conversion values are, however, 0 and 42%, respectively. This is evidence against mechanism 15.

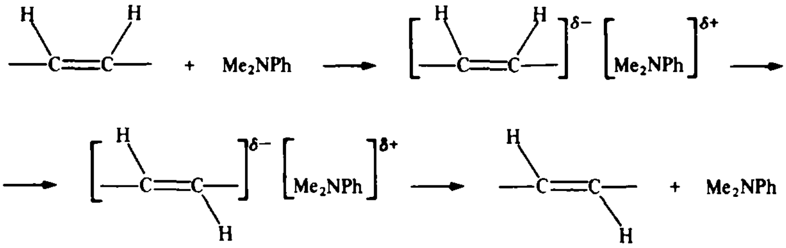
(3) The acidity of the methyne groups in nitrostilbenes is insufficient for dimethylaniline deprotonation (Scheme 15). Besides, α,β-dinitrostilbene is also subjected to conversion and it does not contain methine hydrogen atoms.

(4) The reaction of *cis*-2-nitrostilbene with dimethylaniline in perdeuteroacetonitrile or perdeuterochloroform, as well as the treatment of the reaction mixture (after keeping it without a solvent) with 15% DCl and D_2O, did not lead to H–D exchange. This directly rejects Scheme 15.



Scheme 15.

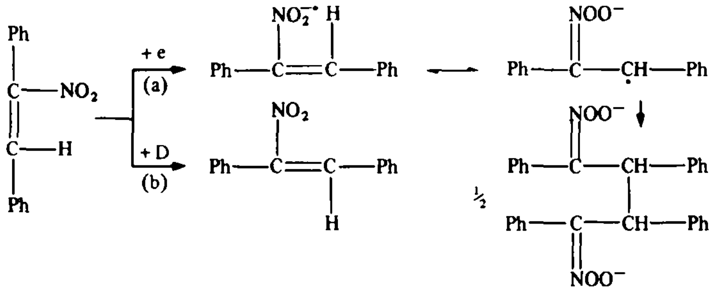
It is also difficult to assume that isomerization observed in this case is related to any artefacts. The effect of impurities, oxygen (the experiments were run in argon), or radicals as in Scheme 2 (iminoxyls do not include isomerization of nitrostilbenes). It would appear that the formation of a complex between the donor and the acceptor has been proved. Apparently, complexation is responsible for the conversion of *cis*-nitrostilbenes into their *trans*-isomers (Scheme 16).



Scheme 16.

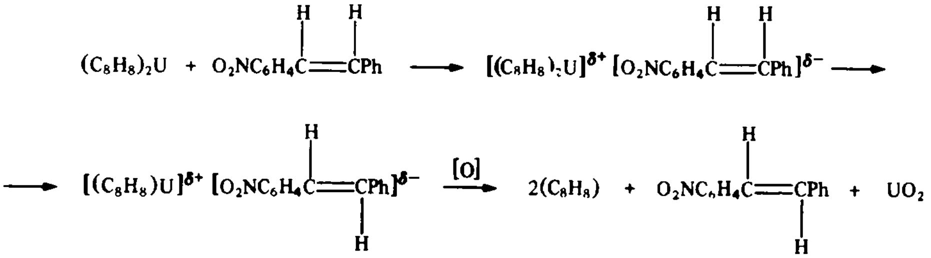
It remains, unclear however, how nitrostilbene in the complex undergoes stereomutation. It is difficult to imagine stereomutation taking place with the lower free orbital of the acceptor populated not by a whole electron but by a fraction of it as suggested by the Mulliken concept.

However, isomerization in a complex still differs from anion-radical isomerization. Anion-radicals of nitrostilbenes undergo conversion instantly whereas in the case of complexes the conversion degree listed in Table 2 is attained within dozens of hours. Some compounds behave differently upon electron transfer and in complexes with a donor. Among them *cis*-α-mononitrostilbene can be mentioned[20,27] (Scheme 17). The reaction follows direction (a) if the cyclooctatetraene dianion is an electron source $(C_8H_8^{2-})$ and direction (b) if the same dianion enters into the composition of a metal complex with thorium or uranium as a central atom.[27] These complexes are of the sandwich type; in the reactions with nitrostilbene there were studied[11,27] thorocene $(C_8H_8)_2Th$, uranocene $(C_8H_8)_2U$, and lanthanocene $(C_8H_8La)K$. The metal complexes enter into donor–acceptor interaction with nitrostilbenes as evidenced by the corresponding charge transfer bands. The nitrostilbene acceptor undergoes *cis* → *trans* isomerization. The effect of steric hindrance in the role of the acceptor and the donor on isomerization was studied. To do this, uranocene, di-*n*-butyl-uranocene, and di-*n*-decyluranocene were compared as donors. *cis*-α-Mononitrostilbene,



Scheme 17.

cis-4-nitrostilbene, and *cis*-α,β-dinitrostilbene were used as acceptors with each of the above three donors. In all donor–acceptor pairs, the degree of *cis* → *trans* conversion of the stilbene component decreased on passing from uranocene to dibutyluranocene and dropped to zero on passing to didecyluranocene. Scheme 18 explains these facts.



$$(C_8H_8)_2U + O_2NC_6H_4\overset{H}{C}{=}\overset{H}{C}Ph \longrightarrow [(C_8H_8)_2U]^{\delta+}[O_2NC_6H_4\overset{H}{C}{=}\overset{H}{C}Ph]^{\delta-} \longrightarrow$$

$$\longrightarrow [(C_8H_8)U]^{\delta+}[O_2NC_6H_4\overset{H}{C}{=}\underset{H}{C}Ph]^{\delta-} \xrightarrow{[O]} 2(C_8H_8) + O_2NC_6H_4\overset{H}{C}{=}\underset{H}{C}Ph + UO_2$$

Scheme 18.

It is noteworthy that no *cis* → *trans* isomerization of stilbenes was observed when didecyluranocene was used as a donor although the formation of a donor–acceptor complex was noticed. The presence of large alkyl substituents in uranocene seems to hinder the interaction of the donor and the acceptor and decreases the degree of charge transfer. Such steric effects were also revealed in other cases of donor–acceptor interaction.[28] One may conclude that the formation of a donor–acceptor complex is a necessary but insufficient conditions for *cis* → *trans* isomerization of the nitrostilbene acceptor. The extent of the conversion also depends upon the degree of interaction between the acceptor and the donor. If their approach is hindered, then the degree of charge transfer naturally decreases. Such a conclusion agrees with the governing principles common for organic and organometallic chemistry. Pointing to the non-absolute nature of stereoindicator tests, the conclusion shows nevertheless their applicability for the evaluation of spatial effects in a series of similarly built organometallic compounds. It is interesting that dibutyluranocene reacts with nitrobenzene under the conditions as in reaction (18) transforming nitrobenzene into azobenzene by Scheme 19. This unusual result was observed[29] and confirmed[11] for 4-methoxyanisole. The same difference between nitrostilbene and nitrobenzene (*cf.* Schemes 18 and 19) is observed when thorocene and lanthanocene are used as donors.

$$(C_8H_8)_2U + O_2NC_6H_4R \longrightarrow [(C_8H_8)_2U]^{\delta+}[O_2NC_6H_4R]^{\delta-} \xrightarrow{[O]}$$

$$\longrightarrow 2C_8H_8 + \tfrac{1}{2}RC_6H_4N{=}NC_6H_4R + UO_2 \qquad R = H, OMe$$

Scheme 19.

It is believed[29] that the initial stage of reaction (19) consists in the formation of a donor–acceptor complex. It is assumed[29] that the central metal atom is attacked by the arene nitro group; as a result, nitroarene is reduced to an azocompound. Under identical conditions [reaction (18)] nitrostilbenes undergo isomerization without the reduction of the functional groups and the total return of *cis*–*trans* isomers is 97–98%. Hence, the transfer of the reaction centre takes place in this case: the substitution of nitrobenzene in the *para*-position with a styryl (but not methoxyl) group protects the nitro group from reduction and results in withdrawal of the excess electron density transferred from donor to the olefinic bond.

From quantum chemical predictions (Scheme 8) it follows that this should really be the case. A comparison of Schemes 18 and 19 also shows that stereoindicators can be used in the experimental verification of those changes in the manner of delocalization of the excessive electron density which are related to the introduction of the olefinic fragment into the acceptor molecule.

Consider Scheme 17 again. The letter D denotes dipyridyltungstentetracarbonyl.[30] The charge transfer bands were found (THF) and *cis* → *trans* conversion of the acceptor was detected. The reaction does not require illumination. In this case, too, no paramagnetic particles were found.

Table 3. *Trans* conversion (C) of *cis*-α,β-dinitrostilbene induced by organometallic compounds with the general formula $(CO)_4ML_2$ [equimolecular ratio, THF, argon, 25°C, 24 h followed by separation into components; a decrease in the amount of $(CO)_4ML_2$ strongly reduces C]

L_2	M/C (%)		
	Cr	Mo	W
$—P(Ph_2)CH_2(Ph_2)P—$	30	26	22
$—P(Ph_2)CH_2CH_2(Ph)_2P—$	40	34	31

Stilbene (the sum of the *cis* and *trans* forms) and the donor are retained completely. Neither pyridine nor carbon monoxide taken separately can cause isomerization of nitrostilbene; isomerization requires joint coordination at the tungsten atom.

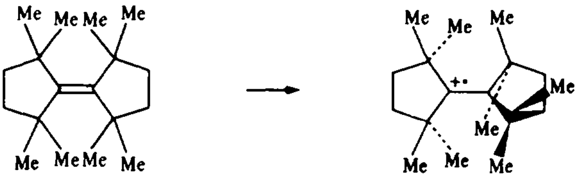
Among other organometallic compounds tetracarbonylphosphine derivatives of the group VI metals were studied.[31] *cis*-α,β-Dinitrostilbene proved to be an active acceptor. The bands of charge transfer between the donor and the acceptor were found and isomerization of the acceptor was disclosed. The ligands taken separately (phosphine or carbon monoxide) do not lead to the conversion of dinitrostilbene either. Table 3 demonstrates the dependence of the conversion degree of this acceptor on the donor structure: the nature of metal M when ligand L_2 is unchanged (horizontal lines) or the nature of the ligand when the metal is unchanged (columns). Thus, a non-trivial approach has been developed for comparing the donor activity of isostructural organometallic compounds by the conversion of one stereoindicator, namely, *cis*-α,β-dinitrostilbene.

The approach can be useful in predicting the catalytic action of organometallic compounds. Catalysis of olefin metathesis with tungsten hexacarbonyl serves as an example.[32] Metal carbonyl $W(CO)_6$ was shown to act as a catalyst and as an electron donor forming donor–acceptor complexes with the substrates. It would be interesting to study more comprehensively the relationship between the catalytic activity of organometallic compounds and their donor ability. Therefore, the stereoindicator method of obtaining the donor scale described above deserves verification using other reactants.

It seems that there can be found organometallic compounds which are able to reduce an acceptor to the anion-radical. The paper[33] supports indirectly such an assumption; it describes the interaction between isonitrile copper derivatives and diethyl maleate. The latter transforms rapidly into diethylfumarate. Metallic copper without isonitrile ligands does not lead to the maleate isomerization. Copper–isonitrile coordination obviously results in a decrease of the metal's ionization potential which then makes possible the electron transfer step. The authors did not find (or did not look for) paramagnetic intermediates in the reaction. However, tetracarboxyethylene (having neither *cis* nor *trans* isomers) gives an anion-radical with a resolved superfine structure under the action of a copper–isonitrile compound. This fact is considered as a proof of the anion-radical mechanism of dimethyl maleate isomerization into dimethyl furmarate. It is noteworthy that such a mechanism, for the isomerization involving electrochemical reduction of maleates, has been established rather rigorously.[34]

3.2. *Ethylenes with introduced positive electron density*

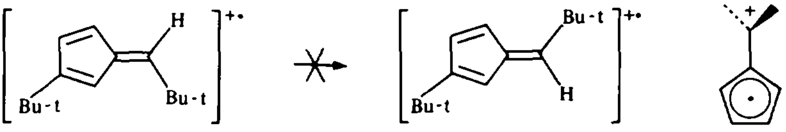
Calculations show[35] that the transformation of tetramethyl- and tetraisopropyl-ethylenes into cation-radicals is associated with some decrease in the energy barrier of *cis* → *trans* isomerization. The barrier, however, remains high enough. For instance, for the ethylene cation-radical the theoretical barrier height amounts to 76 kJ mol^{-1}.[35] It follows from the ESR spectra that in the cation-radical state there is not complete rotation about the ethylene bond (by 180°) but that a twisted structure with the rotation angle of up to 40° is stabilized. It appears that in this case an optimum shielding of the radical and cation centres by alkyl groups (in alkyl derivatives) is ensured. This is observed not only in tetraalkylethylenes but in octamethyl-substituted bicyclopentylidene as well. The latter is oxidized with aluminium chloride to a cation-radical (Scheme 20) which is quite stable in an inert atmosphere.[37] The uncharged molecule is almost planar while the cation-radical, according to the ESR data,[37] has an almost orthogonal arrangement of the 5-membered rings. In other words, the appearance of a spin-positive density permits the rotation of cyclic substituents about the ethylene bond to occur but only to a certain extent in which the methyl groups in the cycles retain their ability to screen the radical and cation centres.[35,37]



Scheme 20.

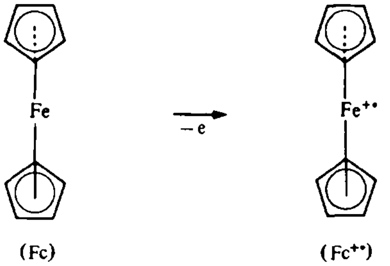
It has been noted[38] that the orthogonal arrangement of the substituents at the olefinic bond favours the effective separation of the unpaired electron and the charge. Such a configuration of a cation-radical makes the return to *cis*-(Z) and *trans*-(E) configurations upon-electron reduction of the cation-radical with the formation of a neutral olefin equally probable. The olefin shown in Scheme 20 is symmetrical and has neither Z nor E isomers. Therefore, the paper[38] which shows that there is no isomerization of cation-radicals of 2,6-ditertbutylfulvenes is of importance (Scheme 21).

The authors[38] believe that this stability is a result of the existence of the cation-radical not in an orthogonal but in a twisted form (Scheme 21). The rotation of the groups in this form is small and this may be due to a specific distribution of spin-positive density in the cation-radical (Scheme 21). In simpler olefins, however, of the stilbene type[39] *cis* → *trans* isomerization in the cation-radical state goes readily.



Scheme 21.

Ferroecenylethylenes are important exceptions in this series. Upon one-electron reduction, following Scheme 9, these compounds isomerize but they show full conformational stability during one-electron oxidation.[19] To analyze this specific feature and the situations responsible for it, one should consider oxidation of ferrocenyl compounds in general. Ferrocences readily lose one electron producing the so-called ferricenium cations which are characterized by an effective localization of the positive charge on the iron atom (Scheme 22).



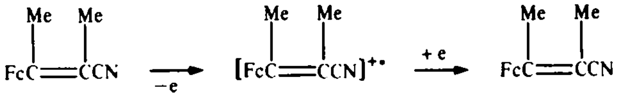
Scheme 22.

The presence of a very strong acceptor or a positively charged substituent on the ferrocenyl nucleus affects the iron atom in the same manner as oxidation of this atom. Such an effect of an acceptor was observed, for instance, in the α-ferrocenyl-β-nitroethylenes.[40] In the course of the formation of α-ferrocenylcarbenium ions, the electronic configuration of the molecule changes so strongly that a new complex is formed containing two different ligands, namely, cyclopentadienyl and fulvenoid.[41] Studies[42] devoted to the behaviour of ferrocenyl analogues of chalcones under electron impact are also interesting. Here radical cations are formed as primary products by Scheme 23.

$$FcR + e \longrightarrow [FcR]^{+\cdot} + 2e$$

Scheme 23.

Chalcones (compounds of the $Ar^1CH{=}CHCOAr^2$ type) lose a hydrogen atom under electron impact after which the CH–CO and Ar–C bonds are cleaved. This is the so-called "chalcone" fragmentation type.[42] The replacement of the phenyl group with a ferrocenyl group in chalcones decreases sharply the contribution of the chalcone fragmentation type to the total fragmentation of molecules of the $FcCOCH{=}CHC_6H_4R$ and $FcH{=}CHCOC_6H_4R$ type. It was shown[42] that the most intense fragment ions are formed as a result of breakdown of the metal–ligand bonds so that, instead of the "chalcone" fragmentation type the "ferrocene" type is observed and the positive charge becomes localized at the metal atom. The aromatic system competes only slightly with the iron atom for the charge. This is confirmed by the high value of the ratio of the total intensity of metal-containing ions (ΣM_i) to that of all ions (ΣFc_i). In $FcCOCH{=}CHPh$ and $FcCH{=}CHCOPh$ $\Sigma M_i : \Sigma Fc_i \approx 0.85$. Localization of the charge at the iron atom is the factor which determines the direction of fragmentation of the above compounds under electron impact in the gas phase. In the liquid phase the cation-radicals of the ferrocene type are characterized by the same factor. This is confirmed by the data[19] on oxidation of ferrocenyldimethylcyanoethylenes. In THF solution $FcC(Me){=}C(Me)CN$ isomers transform tetracyanoethylene into an anion-radical (detected by the typical ESR spectrum). Not cation-radicals $[FcC(Me){=}C(Me)CN]^{+\cdot}$ themselves but their uncharged forms prepared after treatment with water were subjected to analysis. In this case the recovered compounds had the same configuration as the starting materials. Under the conditions of one-electron oxidation at the anode (electrolysis with potential control) in THF against Bu_4NClO_4 cation-radicals are formed quantitatively. After preparation of these cation-radicals, one-electron reduction was performed by changing the direction of the current. According to coulometry data, all the processes were of the one-electron type. As a result, the reactant molecules were recovered without a change in their geometry[19] (Scheme 24).



$$FcC(Me){=}C(Me)CN \xrightarrow[-e]{} [FcC(Me){=}C(Me)CN]^{+\cdot} \xrightarrow{+e} FcC(Me){=}C(Me)CN$$

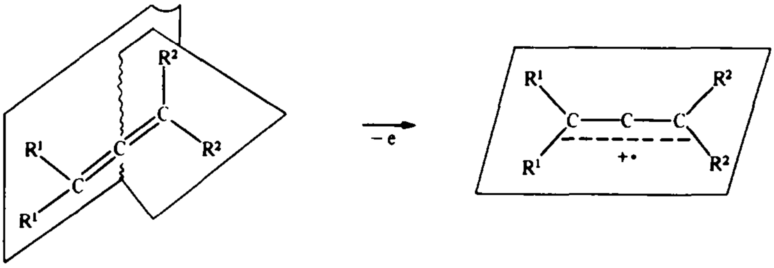
Scheme 24.

It should be noted that the *cis* isomer is thermodynamically less stable than the *trans* isomer. One may assume that in the ferrocenyldimethylcyanoethylene cation-radical the positive charge is localized predominantly at the iron atom. Upon the formation of ferricenium ions of the $C_5H_5Fe^+C_5H_4C(R^1){=}C(R^2)CN$ type, no delocalization of the positive charge with the participation of π-electrons of the olefinic bond takes place. The olefinic bond is responsible for isomerization. This bond is conjugated with the ferrocenyl residue but π-electrons of the olefinic fragment are not shifted towards the central iron atom although the latter is charged positively. In other words, in these ferricenium ions no essential decrease in the barrier of rotation about the olefinic bond takes place and no *cis* → *trans* isomerization is observed.

The fact that in ferrocenylethylene cation-radicals the positive charge is indeed able to be localized at the iron atom is supported by mass spectrometry.[19] The ionization of molecules in the gas phase causes the formation of metal-containing ions whose proportion is rather high. This behaviour is similar to the transformations of the ions from ferrocene and its derivatives when they are generated under identical conditions.[42]

Thus, the transformation of the *cis* form (*Z*) into the *trans* form (*E*) in the ferrocenylcyanoethylene series can be observed only in the presence of negative rather than positive spin density.

In the ferrocenylethylene cation-radical the rotation about the ethylene bond is shown not to occur whereas in the allene cation-radical the rotation is a predetermined process. In the allene molecule there are two cumulated double bonds whose planes are orthogonal. In the allene cation-radical this angle is 30–40°.[43] According to calculations a multiatomic linear cation-radical of allene has a degenerate electron state.[44] Hence, in accordance with the Jahn–Teller theorem, this cation-radical should undergo distortion of the geometry in order to acquire a less symmetric form. It follows from these calculations,[43,45] that the most favourable form is that the angle between the ethylene bond planes of about 40°. This value is close to the experimental data (ESR spectrometry).[43] Allenes containing four *t*-butyl or trimethylsilyl groups at the therminal carbon atoms produce in dichloromethane under the action of antimony pentachloride, such cation-radicals in which an unpaired electron is delocalized along the neighbouring π-bonds[46] (Scheme 25). The conclusion is based on the analysis of ESR spectra with respect to ^1H, ^{13}C, and ^{29}Si.



Scheme 25.

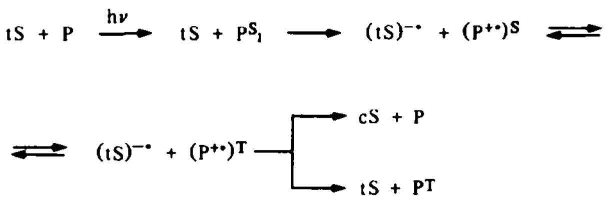
The reactivities of allene cation-radicals and its 1,3-dialkyl, 1,1,3,3,-tetramethyl and 1,1-dimethyl derivatives fully correspond to the structure shown in Scheme 25 (see[46] and refs therein). Thus a fundamental difference between allene (cumulated double bonds are separated) and its cation-radical (cumulated double bonds are conjugated) was established.

Information about the behaviour of olefins acting as donors in donor–acceptor complexes is much scantier than the cases of olefins which act as acceptors. The example provided by Scheme 12 is rather specific. Reactions of stilbenes with iodine, tetracyanoethylene, and chloranil have been described.[47–50] In all these cases donor–acceptor complexes are formed but the complexes from *cis* and *trans* forms are different. It was noted that complexes of methylstilbenes with these acceptors are weak. The charge transfer degree is, apparently, insufficient for isomerization. Stronger acceptors have not yet been studied. The formation of complexes without conversion of the olefinic component was observed. For instance, *cis*- and *trans*-4-methyl- and 4,4′-dimethylstilbenes are reliably detected in the form of complexes with chloranil.[49]

4. REACTIVITY OF ETHENE COMPOUNDS UNDER CONDITIONS OF DONOR–ACCEPTOR INTERACTION

4.1. *Magnetic effects in the reactions of ethenes*

Spin polarization in the photoisomerization of *trans*-stilbene (tS) into *cis*-stilbene (cS) in the presence of pyrene (P) has been observed.[51] The reactions were run in solution (acetonitrile, DMSO or hexafluorobenzene) and the spin polarization was explained[51] using Scheme 26.



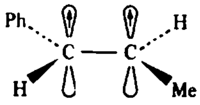
Scheme 26.

According to Scheme 26, the formation of *cis*- and *trans*-stilbenes is preceded by the formation of a magnetosensitive ion-radical by a singlet–triplet conversion. This means that spin polarization must be observed in *cis*- and *trans*-stilbene and the isomerization rate must depend on the magnetic field intensity. These predictions were confirmed experimentally.[51] Hence, the ion-radical route for *cis* → *trans* isomerization is the main one under photoirradiation conditions. This fact enables a new approach to involving sensitized *trans* → *cis* photoisomerization. Up to now the mechanisms assumed for such processes have involved energy transfer and did not take into account donor–acceptor interaction. This interaction makes the process energetically more favourable.[52]

Spin-polarization effects were also observed[52] on photoisomerization of phenylvinyl ether, phenylpropene, stilbene, and 4,4′-dimethoxystilbene in the presence of the sensitizers: dicyanoanthracene, dicyanoethylene, chloranil, phenanthrene, and 9-cyanophenanthrene. In all these cases spin-polarization was observed both in a converted and a non-converted olefin. There is an important feature of the process which was not mentioned before: the olefin recovered without isomerization reveals spin polarization to a greater extent than the converted olefin.[52] This feature fits adequately in the ion-radical conversion mechanism. Indeed, this mechanism implies that an ion-radical pair is formed on the main route of the reaction. The ion-radical pair can then return to the initial state giving rise to the non-isomerized initial olefin. The return to the initial state by the reverse electron transfer from the anion-radical of the acceptor to the cation-radical of the donor (olefin) takes place in the pair caged by solvent molecules. Thus, recombination of the components of the pair proceeds prior to their emergence from the cage into the solvent medium. In other words, the olefin after such recombination is recovered completely spin polarized. There are, however, such pairs which do not recombine but separate into free ion-radicals and emerge into the bulk of the solution. In the bulk the cation-radicals of the olefin isomerize and (or) exchange electrons with non-reacted molecules of the initial olefin. Such an electron exchange is accompanied by a scattering of spin polarization so polarization of the isomerized olefin becomes weakened. This reasoning is completely applicable to the ion-radical pairs which possess lower energy than the triplet states of the reagents and products. Under this condition, recombination (electron exchange) takes place in the singlet pair and gives rise to the initial compounds in the ground state. The pair of the chloranil anion-radical with the phenylpropene cation-radical is a typical example of such a pair.[52] If chloranil is replaced with tetramethyl-*p*-phenylenediamine, the role of phenylpropene in the photoinduced process changes: it gives not a cation-radical but an anion-radical (in a pair with the diamine cation-radical). The energy of this pair is higher than that of the triplet states of the reagents and products.[52] Of course, both singlet and triplet ion-radical pairs are capable of a reversible electron transfer. The difference (a very essential one) between these pairs consists in that a singlet pair recovers the initial compound in the ground state whereas recombination of a triplet pair gives equal proportions of the ground and triplet states. Since a portion of the neutral olefin mentioned here returns in a triplet state, its steric features should be considered. Scheme 27 shows that this state, as long as it exists, should be characterized by orthogonal geometry. In this case the overlapping of the orbitals with unpaired electrons is minimal so a triplet state can exist.

cis
(triplet)

intermediate
(triplet state)



trans
(triplet state)

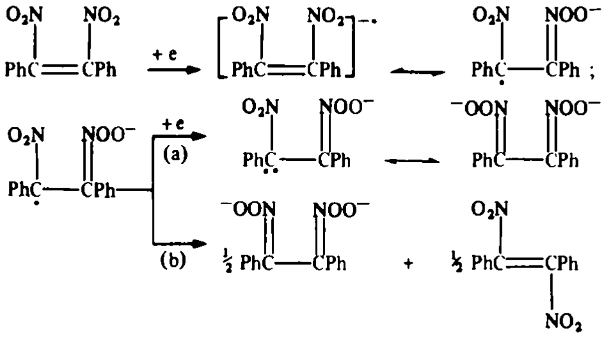
Scheme 27.

Being orthogonal, the triplet state may be transformed into the ground state with both *cis* and *trans* configurations regardless of the geometry of the ion-radical from which the triplet was formed. Since the energy of the triplet state is lower than that of the ion-radical pair, the formation of the triplet is more essential than the emergence of the ion-radical into the bulk and a subsequent exchange of an electron with a neutral molecule. Hence, the scattering of spin-polarization is not intense in this case and the product of isomerization gives a strong CIDNP effect. Experiments[52] support this statement.

4.2. *Stereochemistry of ethene reactions as a reflection of the donor–acceptor mechanism*

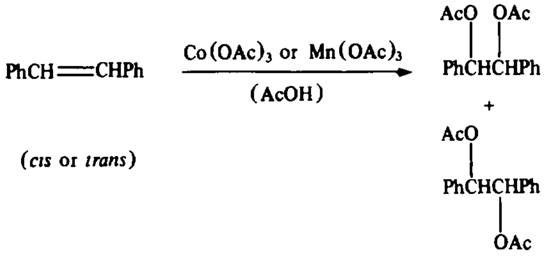
If ethenes enter into a donor–acceptor interaction and if this interaction lies on the reaction coordinate then one may expect the manifestations of the interaction both in the spatial structure of the products and in the isomerization of the initial substrates.

Isomerization of the initial substrates was considered above (Schemes 9 and 11). The diagnostic approach of this type makes it possible to reveal a detectable one-electron stage in a multielectron liquid-phase process. One-electron reduction of *cis*-α,β-dinitrostilbene yields an anion-radical which is stabilized in a nitronic form with a carboradical centre. These radicals possess an enhanced electron affinity and are prone to the capture of the second electron with the formation of a stable dinitronic dianion [Scheme 28, direction (a)]. The radicals can, however, undergo disproportionation without a further reduction along direction (b), Scheme 28. It is important that direction (b) should lead not to one but to two stable products, namely, dianion and uncharged dinitrostilbene. The latter should acquire a configuration different from that of the initial substrate. This was really the case in the experiment[53] (dipotassium cyclooctatetraene as an electron donor and THF as a solvent).



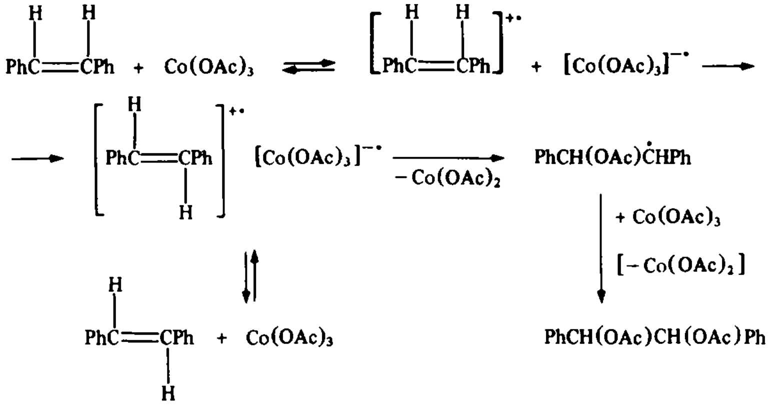
Scheme 28.

In papers[18,54] acetoxylation of stilbene with cobalt and manganese triacetates (Scheme 29) was considered from the standpoint of the geometry of the recovered substrate and the stereochemical composition of the product obtained. ESR studies have shown that in the course of the reaction the cation-radicals of stilbene are accumulated and then consumed. The stereoisomeric composition of the final product is constant and does not depend on the configuration of the initial substrate. Acetoxylation of the olefin bond in *cis*-stilbene is almost by one order of magnitude slower than in *trans*-stilbene. If *trans*-stilbene was the initial compound then the unconsumed part was recovered without any configuration change. When *cis*-stilbene was used as the initial reagent then the recovered olefin was a mixture of *trans* and *cis* isomers. Hence, the *trans* configuration is more favourable for oxidative acetoxylation than the *cis* configuration. In accordance with this conclusion, a mechanism was proposed shown in Scheme 30.



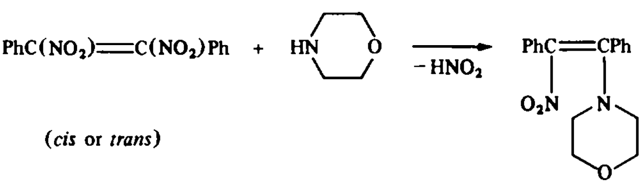
Scheme 29.

It is seen that the cation-radical of stilbene and not stilbene itself is subjected to acetoxylation. *trans*-Stilbene yields the *trans* form of the cation-radical which then enters directly into further reaction. *cis*-Stilbene gives a cation-radical with a *cis* structure which at first acquires the *trans* configuration and only after that adds the acetate ion.



Scheme 30.

A similar approach was taken in detecting the donor–acceptor mechanism for the replacement of the nitro-group with morpholine in α,β-dinitrostilbene.[55] Scheme 31 illustrates the overall results of the reaction. Neither anion-radicals nor dianions of α,β-dinitrostilbene are formed in the system. The reaction proceeds very rapidly and the donor–acceptor complex cannot be detected by the spectral method. The unreacted portion of stilbene returns in a *trans* form (if *cis*-dinitrostilbene was used as the initial reagent) which means that *cis* → *trans* conversion occurs. The yield of the final product grows with a decrease (and not with an increase) in temperature. This suggests that initially a donor–acceptor complex is formed by the reagents. In a similar way the same substrate produces a complex with dimethylaniline (Table 2) but, because of steric shielding of the amino group, the reaction involves only *cis–trans* isomerization of the substrate without substitution. The substitution shown in Scheme 31 proceeds either directly in the donor–acceptor complex or involves the rearrangement of the latter into the addition product which then stereospecifically splits off nitrous acid. The formation of the same *cis* product regardless of the substrate configuration may be either the result of a stereospecific cleavage or an increased thermodynamic stability of *cis*-nitramine. It is the *cis* form in which conjugation of the amino and nitro groups through the olefinic bond is most effective.



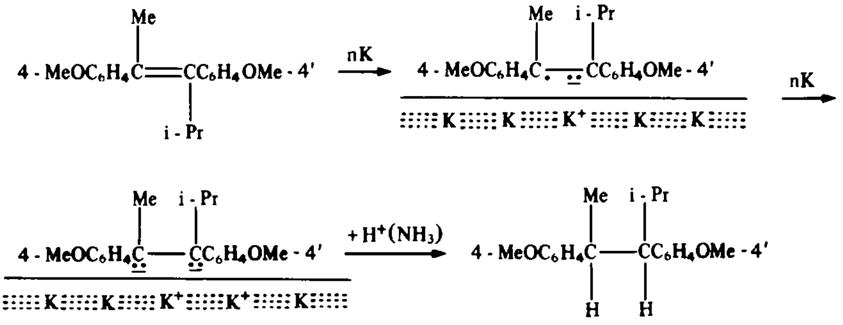
Scheme 31.

It should be noted that the temperature factor in the reaction (Scheme 31) is negative. Such an effect is usually observed when the pre-reaction stage required for the formation of the product involves the formation of a donor–acceptor complex. Chlorination of ethylene is a typical example.[56] For the complex to be formed, the reagents should be kept near one another, that is their mobility in solution should be low. A decrease in temperature lowers the free path of the molecules and favours an intermolecular interaction. Therefore, the fact that the formation of the product is promoted by the cooling of the reaction medium points to the participation of the donor–acceptor complex in the process of addition.[56] The negative temperature factor has diagnostic significance.

4.3. *Control of the reactivity of ethene compounds based on their participation in donor–acceptor interaction*

This Section will deal with the results of enrichment of ethene compounds with electron density and then with its depletion.

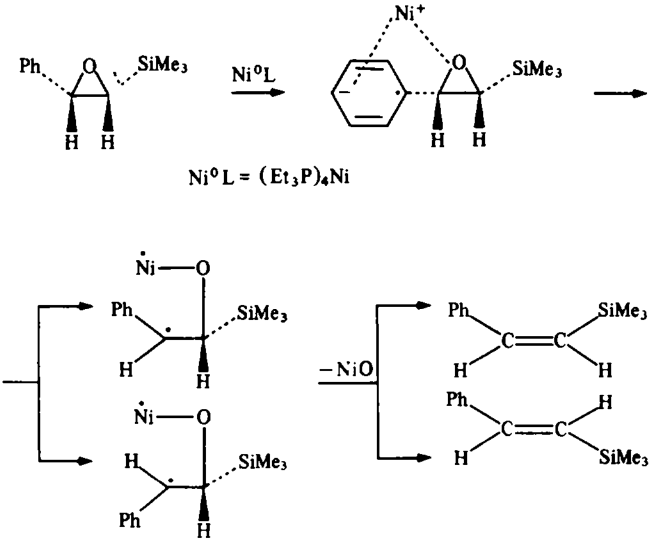
Stilbene derivatives can be reduced with alkali metals in liquid ammonia. The reaction is usually performed in a homogeneous medium to give substituted diphenylethane compounds as a mixture of stereoisomeric forms. However, there are compounds (e.g. biologically active compounds) for which the stereospecificity of the synthesis has a decisive importance. A simple modification of the method of reduction with an alkali metal in liquid ammonia has been found[57] which makes it possible to perform the process stereospecifically. The metal is not predissolved, as usual, but is added in small portions without trying to make the reaction medium homogeneous. Stereoselectivity is ensured by the reduction proceeding not in the bulk but on the surface of the metal. The process is shown in Scheme 32.



Scheme 32.

Adsorption forces cause α-methyl-β-isopropylstilbene (simultaneously with electron transfer) to be arranged in such a way that the substituents at the olefin bond deviate from the metal surface. Reaction (32) is completed by the addition of two protons to the dianion from the metal side. Therefore, regardless of the configuration of the initial olefin, the reduction proceeds with a predominant formation of the erythro-product.[57]

In paper[58] another simple example of a technique controlling the stereoisomeric composition of the reaction product is shown. The technique consists in changing the time of contact between the reagents. Scheme 33 illustrates the transformation of β-trimethylsilylstyrene oxide into β-trimethylsilylstyrene under the action of complexes of zero-valent nickel. The reaction involves oxidation of the complex-bonded metal.[58]



Scheme 33.

It is seen from Scheme 33 that simultaneously with nickel oxidation the epoxy ring is cleaved and the Ni–O bond is formed. This results in the formation of a biradical in which the groups can rotate freely. The cleavage of the nickel-containing radical yields a mixture of olefins and nickel oxide. At early reaction stages (30 min), *cis-* and *trans-*olefins are formed in approximately equal amounts. After a prolonged contact (30 h) when all possible transformations should be completed, the *trans* isomer is the main product and a *cis–trans* ratio equal to 5:95 is established. Such an enrichment of the mixture with the *trans* isomer follows from the previous discussion: the olefin formed interacts with an excess of the nickel complex. The *trans* isomer remains unchanged whereas the *cis* isomer is converted into the *trans* form. The mixture thus becomes enriched with olefin having the *trans* configuration. In a reference experiment[58] the treatment only of *cis*-β-trimethylsilylstyrene with a zero-valent nickel complex resulted in a 85% conversion into the *trans* isomer.

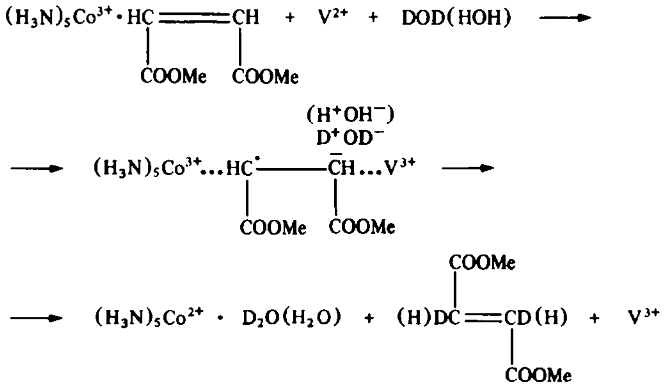
Taube and Fraser[59] studied the interaction of Cr^{2+} or V^{2+} ions with complex salts containing a cation of methylmaleatopentamminocobalt. In an acidic medium ($HClO_4$) a redox reaction takes places as a result of which the positive charge in the complex cation decreases by unity and the complex cation exchanges water for the methylmaleate ligand (Scheme 34).

$$[Co(NH_3)_5(CHCOOMe)_2]^{3+} + Cr^{2+}(\text{or } V^{2+}) + H_2O \xrightarrow{HClO}$$

$$\longrightarrow [Co(NH_3)_5H_2O]^{2+} + Cr^{3+}(\text{or } V^{3+}) + (CHCOOMe)_2$$

Scheme 34.

The liberated ligand is hydrolyzed in the acidic medium to ethylene-1,2-dicarboxylic acid. However, not all the diacid formed has the *cis* configuration corresponding to the ligand in the initial complex. Along with maleic (*cis*) acid, fumaric (*trans*) acid is also formed. The amount of fumaric acid formed is the greater, the higher concentration of perchloric acid in the reaction mixture. In the presence of D_2O a mixture of isomeric acids is obtained; the C–D bonds are detected only in fumaric but not in maleic acid. The reduction of the methylfumaratopentamminocobalt ion in D_2O (Scheme 34) yields only fumaric acid without maleic acid: this fumaric acid does not contain C–D bonds. Evidently, the electron transfer from Cr^{2+} or V^{2+} to the complex ion is accomplished by the so-called double exchange mechanism. The reductant (Cr^{2+} or V^{2+}) transfers an electron to the bridge group (maleate) and the latter to the oxidant (Co^{3+}). Thus, the bridge $(CHCOOMe)_2$ group is reduced and oxidized alternately. This is accompanied with isomerization of *cis*-ethylenedicarboxylic ester into its *trans* form. When an electron is localized at the ethylene bond, the addition of a proton (deuteron) takes place. After removal of the electron from the ethylene bond an H^+ ion (in H_2O) or H^+ and D^+ ions (in D_2O) are also detached. Isotopic hydrogen exchange at the —C═C— bond is observed. The conversion of Co^{3+} into Co^{2+} proceeds simultaneously with the replacement of the ethylenedicarboxylic acid diester with a water molecule in the inner sphere of the complex (Scheme 35).



$$(H_3N)_5Co^{3+}\cdot \underset{COOMe}{HC}{=}\underset{COOMe}{CH} + V^{2+} + DOD(HOH) \longrightarrow$$

$$\longrightarrow (H_3N)_5Co^{3+}\ldots \underset{COOMe}{HC^{\bullet}}\text{—}\overset{\substack{(H^+OH^-)\\ D^+OD^-}}{\underset{COOMe}{\bar{C}H}}\ldots V^{3+} \longrightarrow$$

$$\longrightarrow (H_3N)_5Co^{2+}\cdot D_2O(H_2O) + (H)\overset{COOMe}{DC}{=}\underset{COOMe}{CD}(H) + V^{3+}$$

Scheme 35.

The absence of an isotopic hydrogen exchange at the C atoms of the ethylene bond in the dimethylfumarate ligand may be due to the fact that in this case the bridge does not participate directly in the process of electron transfer. The role of the ligand resides most likely in the converging of two positively charged ions for a "direct electron exchange" between the overlapping orbitals of these ions. A similar reaction of electron exchange between Ru^{4+} and Ru^{5+} was performed in a complex containing both ions as coordinating centres.[60] 1,4-Dipyridylbutadiene-1,4 in a *cis* or *trans* form is a conducting system: stereochemical changes of this bridge occur when an electron passes on it can be used, it is believed,[60] in forming a molecular switch.

In addition to the anion-radical reaction of stilbene photoisomerization shown in Scheme 26, consider now a cation-radical reaction. It was found[61] that photoirradiation of *cis*-stilbene (cS) in the presence of 9,10-dicyanoanthracene (DCA) with 365 nm light at 25°C yields *trans*-stilbene (tS). This photosensitized process is facilitated by the following factors: the replacement of a non-polar solvent (benzene) by a polar one (acetonitrile), reaction temperature rise, an increase of the stilbene concentration, a decrease of the irradiation intensity, or the addition of salts of alkali metals. All these factors intensifying the process are directly related to the mechanism shown in Scheme 36. Let us analyze the effect of these factors on the efficiency of the photoreaction (Scheme 36). An increase in the cS concentration favours the propagation of the chains and decreases the probability of their termination when $(DCA)^{-\cdot}$ reacts with $(t, cS)^{+\cdot}$. A decrease in the irradiation intensity has a similar effect: the chain propagation is a first-order process, whereas termination of the chains is the second-order process. Temperature rise accelerates the accumulation of cation-radicals $(t, cS)^{+\cdot}$; in this system the free energy of electron transfer is from -53 to -44 kJ mol^{-1} (the transfer is in fact an endothermal process). An increase of the isomerization when passing from a non-polar solvent to a polar solvent is due to the fact that the $(cS)^{+\cdot} \rightarrow (tS)^{+\cdot}$ conversion goes more readily with free cation-radicals than with ion-radical pairs (with exiplexes). The $(S)^{+\cdot}$ cation-radical not shielded with a counterion has a more positive charge and therefore becomes stabilized in a more polar solvent. In other words, isomerization is less effective when $(cS)^{+\cdot}$ forms an ion pair with $(DCA)^{-\cdot}$. When $NaClO_4$ (salt of an alkali metal) is added, the $(DCA)^{-\cdot}$ anion-radical becomes bonded in another (more compact and therefore more stable) ion pair, $(DCA)^{-\cdot}Na^{+}$. As a result, the $(cS)^{+\cdot}$ cation-radical is liberated. In addition, chain termination caused by interaction of $(S)^{+\cdot}$ with $(DCA)^{-\cdot}$ becomes less probable because the cation-radical and the anion-radical are not so close to each other as in a united ion-radical pair.

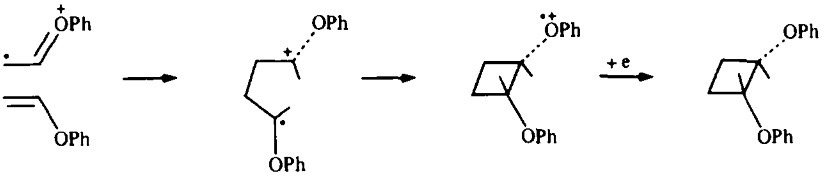
$$cS \xrightarrow[-(DCA)^{-\cdot}]{+DCA} (cS)^{+\cdot} \longrightarrow (tS)^{+\cdot};$$

$$(tS)^{+\cdot} + cS \longrightarrow tS + (cS)^{+\cdot} \text{ etc.};$$

$$(DCA)^{-\cdot} + (t,cS)^{+\cdot} \longrightarrow DCA + t,cS$$

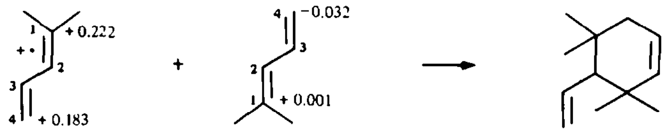
Scheme 36.

The cation-radicals of ethenes which are the primary products of donor–acceptor interaction differ in their reactivity from the corresponding neutral compounds. This widens the possibilities of syntheses on the basis of ethenes. Primary oxidation of ethenes (photochemical) with salts of transition metals or amminium salts of the $(4\text{-}BrC_6H_4)_3N^{+\cdot}ClO_4^-$ type makes it possible to obtain cation-radicals which initiate reactions which are unusual for ethenes in an uncharged state. For instance, the cation-radicals of phenylvinyl ether initiates[62–65] head-to-head dimerization according to Scheme 37. Dimerization is attained by the addition of a cation-radical to an olefin in a neutral form; the chain of transformations ends by a one-electron reduction of the cation-radical of a cyclic dimer. Unreacted phenylvinyl ether then acts as a one-electron donor and the transformations continue. In similar pericyclic reactions up to 500 units fall per cation-radical can occur. Thus, even dienes with a shielded double bond can be involved into diene synthesis. The presence of donor groups at the double bond normally hinders the participation of the double bond in such reactions. The reaction does, however, take place with cation-radicals. Cyclic adducts are formed in high yields (80–90%) and under mild conditions. Polymerization which usually decreases the yield is inhibited completely.[66] Stereoselectivity of the addition, typical of diene condensation, does not change in the cation-radical version and even grows. The position and regioselectivities also grow. These effects have been studied in a series of papers.[66–71]



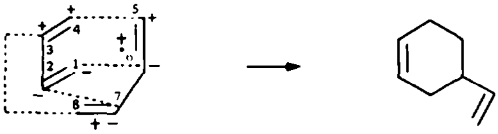
Scheme 37.

The position selectivity is observed in those cases where a non-symmetrically substituted diene acts as the dienophile. The more substituted double bond is involved in ion-radical reactions according to Scheme 38. Regioselectivity is possible when both the diene and the dienophile are non-symmetrically substituted. Then dimerization can be of the head-to-head type with the formation of 1,2-disubstituted derivatives of cyclohexene or of the head-to-tail type if cyclohexene with substituents at positions 1 and 3 is formed. In the ion-radical synthesis condensation of the head-to-tail type is more typical (Scheme 38). Stereoselectivity manifests itself in condensation of a diene with a diene; the double bond which remains free may deviate from the ring formed (*exo* configuration) or approach it (*endo* configuration). *Endo* condensation is a predominant direction of the ion-radical reaction (Scheme 39). All the observed manifestations of selectivity are seen in Schemes 38 and 39.



Scheme 38.

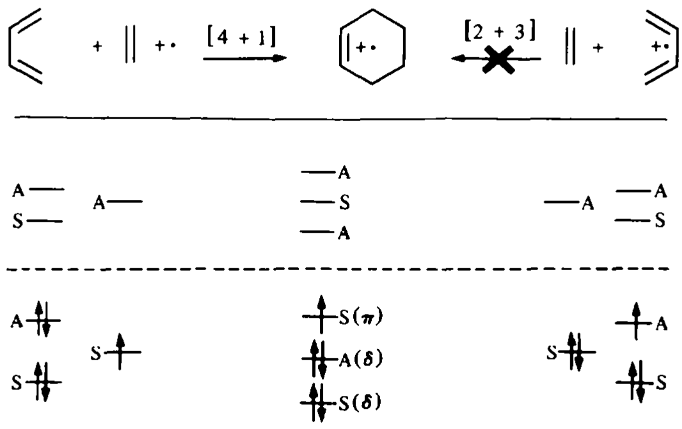
Scheme 38 shows how the charge distribution in reagents dictates the head-to-tail reaction with the participation of the multiple bond of the dienophile which is substituted participating to the greater extent. For the cation-radical the position selectivity at the C-1 atom is 100%, regioselectivity being zero, whereas at the C-4 atom the position selectivity is zero and regioselectivity is 100%. In other words, the addition of the $D_1^{+\cdot} + D_4^{\circ}$ type is only observed (symbol D° refers to a neutral diene and $D^{+\cdot}$ to a diene in a cation-radical form).



Scheme 39.

The cation-radical version of the diene synthesis, in which the diene is in a strongly electron-deficient state, is characterized by an unusual high endoselectivity. It follows from Scheme 39 that when a cation-radical and a neutral molecule approach each other only the C_1–C_6 and C_4–C_5 interactions are bonding and this results in cyclization. It is important that the C_2–C_7 and C_3–C_8 interactions are also bonding. This favours the "bending down" of the extra-nuclear propenyl group to the cycle so that the *endo*-product is formed. Generally speaking, diene condensations also proceed with the predominant formation of *endo*-adducts when neutral molecules participate in the interaction. In the cation-radical version endoselectivity increases sharply. This is quite understandable: the cation-radical acts as an independent particle and the contribution of the suitable molecular orbital of the cation-radical becomes determinant.

The papers[66–71] which were reviewed above deal only with reactions in which a cation-radical acted as the reagent. However, there can be cases where a cation-radical is formed in the course of donor–acceptor interaction between initially neutral molecules. Then the rigid or sharply increased selectivity of the reaction acquires a diagnostic significance. For such examples, there is a general rule: condensation is permissible only for the dienophile cation-radical + diene pair and forbidden for the dienophile + cation-radical of a diene pair. This tendency can be understood from the orbital correlation diagram shown in Scheme 40; symbols S and A denote symmetric and antisymmetric orbitals. It is seen from Scheme 40 that the interaction between the orbitals of equal symmetry (which is the condition of the condensation under consideration) is possible only when the diene supplies four electrons and the dienophile one electron. If the diene supplies three electrons and the dienophile supplies two electrons then no cyclic adduct can be formed. This is shown in the Scheme (40), the [4 + 1] process goes and the [3 + 2] process does not take place. Upon one-electron oxidation, cation-radicals both of the diene and the dienophile can be formed. Each of these cation-radical can exchange an electron with any participant in the reaction. But since only diene cation-radicals are bonded into the adduct, the equilibrium of the electron transfer is gradually shifted towards this particular cation-radical.



Scheme 40.

5. CONCLUSION

Ethene compounds are suitable for establishing various aspects of the donor–acceptor nature of the interactions which are observed. This statement is based upon two main properties of the ethene bond: the ability to be opened under the attack of particles of the radical character and the tendency to rotation upon charge transfer (negative or positive). Ethene compounds introduced into the reaction systems can be incorporated into the structure of the final product. They also may act as stereoindicators characterizing the donor (acceptor) ability of the reaction participants. The review has also dealt with transformations of ethene compounds proper. It is shown how and why one can control these reactions if they follow the donor–acceptor route. The response of the reaction system to the electronic constraints supports, in its turn, the above mechanism. All these factors allow us to consider ethene probing as an essential tool for studying the mechanism of organic and organometallic reactions of the donor–acceptor type.

Different methods (not including ethene probing) used in studying the mechanism of the above-mentioned reactions have already been analyzed in the literature.[72] The state of the art and the prospects of further investigations in this important field have been assessed.[73] The results obtained show that this field is now at a stage of using the ideas which have been developed. But the influx of new ideas is prolonged.

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