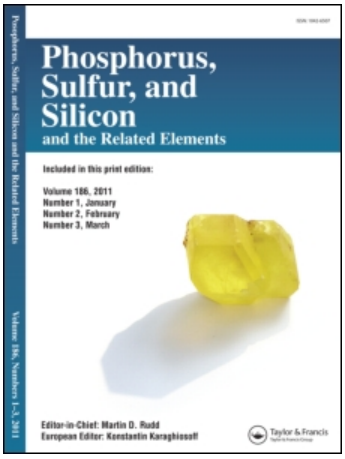

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REVIEW ARTICLE

The Role of the Electron Transfer Stage in Reactions of Organo-sulfur Compounds and the Problem of Directed Influence on These Reactions

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The importance of the electron transfer stage for conversions of organo-sulfur compounds is demonstrated. The factors are analyzed allowing one to realize specific influence on these conversions, viz. to initiate the conversions by facilitating the stage associated with ion radical formation, to alter their direction by varying the solvent nature or the state of ionic aggregates. It is emphasized that the above mentioned ways to exert influence possess a rather general application. The bibliography contains 27 references.

1 INTRODUCTION

The electron transfer stage is widely met in chemical conversions and even more widely in biochemical processes. Among the latter are bioconversions occurring in respiratory chains and transformations such as cystine-cysteine. It is the electron transfer reactions which provide the basis for synthesis of sulfoxides from thioethers or disulfides from thiols.

For an organic compound to be involved in an electron transfer reaction very many conditions are needed related to electronegativity and ionization potential values, as well as to bond polarizability in the given compound.

Organo-sulfur compounds possess a number of features which make them predisposed toward electron transfer reactions. Sulfur polarizes much more easily than other atoms. The polarizability of sulfur is about twice that of carbon and about five times as great as that of oxygen; the C—S bond polarizes twice as easily as does the C—C bond and two and half times as easily as the C—O bond[1] (see Scheme 1).

The presence of the C—S bonds lends stability to the ion radical forms of a molecule. Thus aromatic thioethers yield simultaneously both cation and anion radicals as stable particles.[2] By contrast, if no sulfur-containing groups are present the existence of cation and anion radicals of the same molecule is observed only in few cases.

Polarisability (P)

Atom	P, Å^3	Bond	P, Å^3
S	3,45	C-S	1,9
C	1,75	C-C	1,0
O	0,73	C-O	0,8

Scheme 1

Most organo-sulfur compounds are known as powerful electron acceptors. Among them are disulfides, sulfene chlorides, sulfene amides, sulfene ethers, thiocyanates.[3] On the other hand, thiols can behave as effective donors. They exhibit a larger affinity for radicals than do other nucleophiles.[4] Organo-sulfur groups carrying excess charge are predisposed toward coordination.[5] Based on Ref. 6 sulfur is, in general, a soft base and along with high polarizability features low electronegativity and facile oxidizability. A distinctive feature of sulfur is the presence of unoccupied orbitals which lie not very highly (with oxygen, for instance, they are completely absent).

Thus organo-sulfur compounds, thanks to their own nature, are capable of participating in reactions involving electron transfer. There was no possibility to review all such reactions in a single paper. So, only the most important examples were

selected. It turned out, in fact, that the most interesting were the reactions representing nucleophilic or electrophilic substitution. By pure accident, most compounds considered in the review are bivalent sulfur derivatives. The principal aim of the review is not, of course, to consider one or another organic derivative of sulfur. The aim is to make an analysis of the phenomena governing the reactions of these compounds. In doing so, we shall select those reactions which involve the electron transfer stage and consider the ways of directed influence, affecting precisely this stage. So, we shall deal with no particular substances but only with the phenomena.

2 THE ELECTRON TRANSFER STAGE IN SUBSTITUTION REACTIONS OF ORGANO-SULFUR COMPOUNDS

Let us consider the general scheme, for instance, of nucleophilic substitution. Nucleophilic Y^- gives off an electron to substrate RX to yield nucleophile radical $Y^\cdot$ and substrate anion radical RX^-. The subsequent course of the reaction depends on what will happen with the substrate anion radical RX^-. It can undergo decomposition or enter into combination with ions and radicals without decomposition[7–11] (Scheme 2).

The conversions proceeding without decomposition of the substrate anion radical involve intermediates containing a tetrahedral carbon. Such reactions are usually classified as S_N2 processes. The above intermediates can appear both via coupling to give a biradical pair and after going out from the solvent cage, followed by attack by one more mole of the reagent. The reactions of the type $S_{RN}1$ involve the cleavage of the ionic group X^- from the parent ion radical and subsequent addition of the reagent at the free valency site.

The possibility that coupling may yield the biradical pair without going out from the solvent cage is difficult to examine because of the absence of reliable methods. Therefore the confirmation or rejection of the biradical mechanism for substitution is a matter for the future.

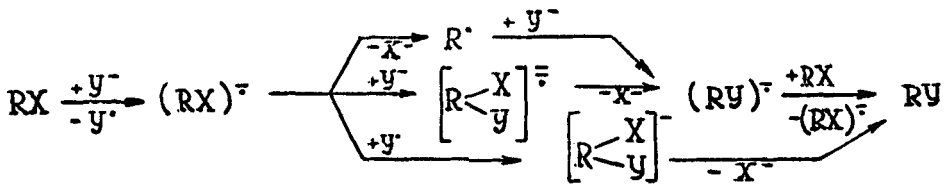
The reactions involving the outgoing of the electron transfer products into the bulk of solution or the formation of secondary radicals more readily lend themselves to investigations. These reactions are now attracting much attention and a few results have been accumulated, of importance both in the theoretical and practical respects. The development of such investigations seems to be urgent as they provide the methods for producing required final substances or for increasing the yield and rate of their formation.

In studies of substitution at a saturated tertiary carbon Kornblum[12] compares the reactions of α-cumylchloride and *p*-nitro-α-cumylchloride with the thiophenolate ion. The difference lies in the nature of the resulting products, as is shown in Scheme 3.

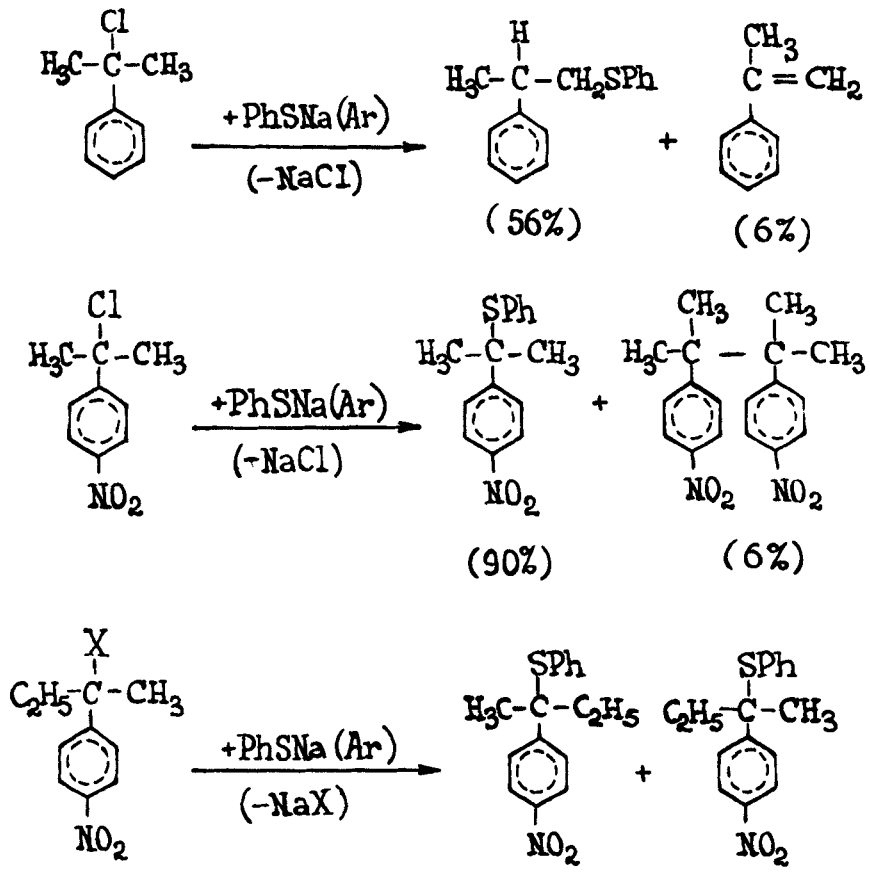
Only those cumyl compounds undergo the substitution which contain a nitrogroup in the para position. The reaction occurs equally well with both small and bulky anions. Thus a moiety can be incorporated containing naphthyl nuclei and other bulky fragments. It is noteworthy that the optically active substrate yields, on interaction with sodium thiophenolate, a substitution product in the racemic form[7] (Scheme 3). The addition of radical inhibitors prevents formation of substitution products. Oxygen drastically retards the substitution reaction but favors the formation of *p*-nitrocumylperoxide. Light exerts strong initiating influence. Consequently, we deal here with a reaction of the radical type.

The reaction leading to substitution starts with electron transfer from the thiophenoxide ion to the nitro compound. The thiophenolate ion plays here the role not only of a one-electron donor but also of a scavenger of radicals appearing at one of the intermediate stages. The foregoing is illustrated in Scheme 4.

The Scheme allows one to realize two characteristic features of the reaction: its applicability to



Scheme 2

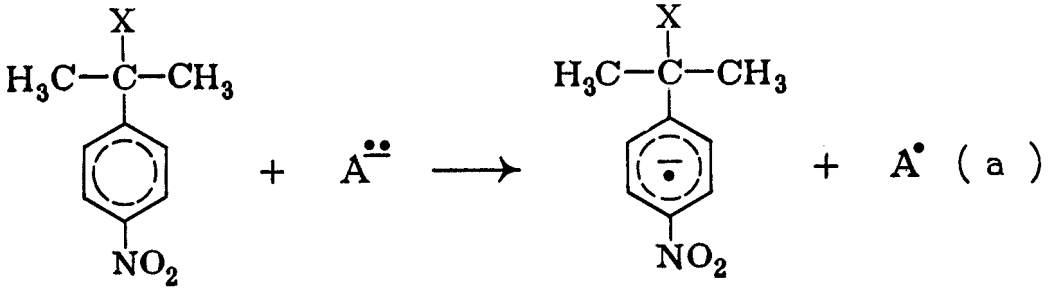


Scheme 3

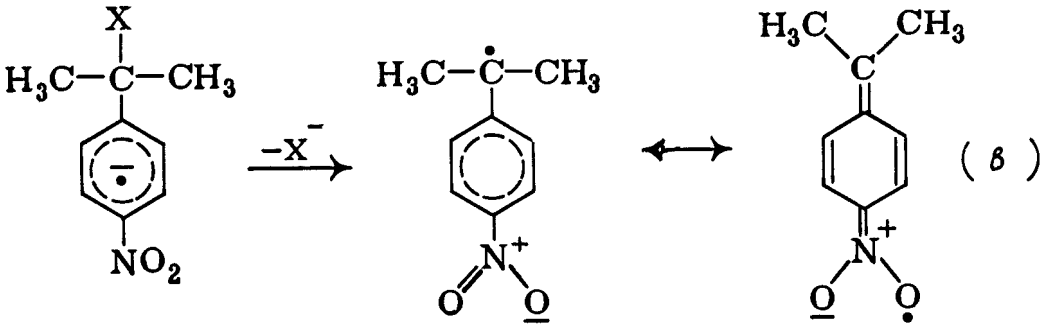
p-nitrosubstituted substrates only and its insensitivity to steric factors. The presence of a nitro group in the para position brings about delocalization of the excess electron and thereby favors anion radical formation (stage a of Scheme 4). Stage (a) is related to a non-eclipsed nitrophenyl fragment of the *p*-nitrocumyl system and steric hindrance is here insignificant. Stage (b) of Scheme 4 represents intramolecular elimination and is not controlled by steric effects as well. Stage (c) of Scheme 4 involves addition of anion A^- (particularly, of PhS^-) to the planar system of the free radical. The free radical features high reactivity and is accessible to attack by the anion. Hence, stage (b) of Scheme 4 can be rapid; this is of great importance since it is stage (b) that leads the chain of conversions. It is essential for the chemistry of organo-sulfur compounds that the thiolate ions are extremely effective radical scavengers as compared with other nucleophiles.

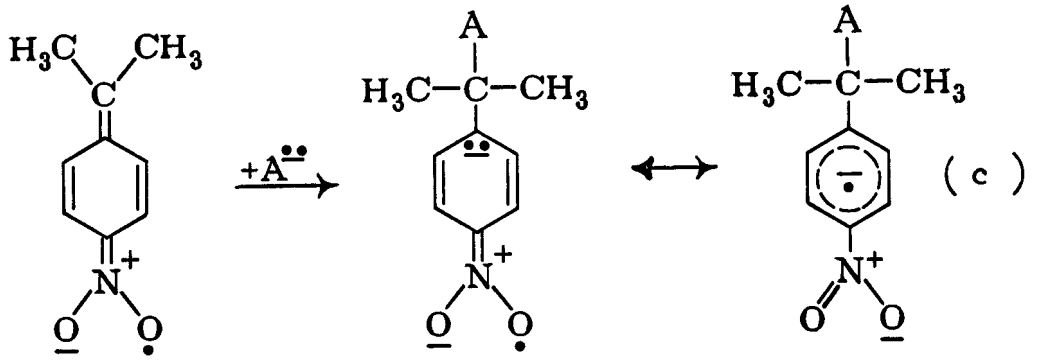
As has been exemplified by the reactions of 5-chloro-2H,3H-benzo[b]thiophene-2,3-dione with nucleophiles, it is only in the case of phenylthiolate where substitution of chlorine by the PhS group takes place, while with phenoxy or hydroxy ions there proceeds merely reductive dechlorination (Scheme 5). This means that it is the thiophenolate which scavenges the intermediate σ-radicals.

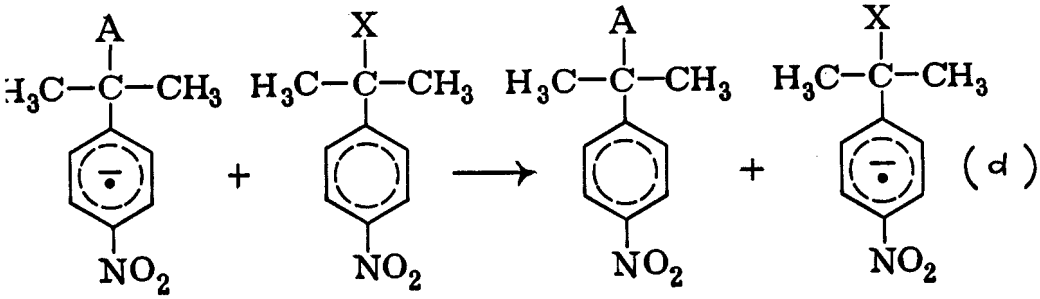
A mechanistic study of thioarylation of 9-bromo-9-phenylfluorene[13] has also confirmed that the radical stage must be taken into consideration in nucleophilic substitution. When treated with sodium thiophenolate in dimethylformamide (DMF) under nitrogen the above bromo derivative yields sodium bromide and 9-phenylfluorene (Scheme 6). The sodium bromide is obtained quantitatively whilst the yield of the nucleophilic substitution product amounts to only 42%. The substrate and nucleophile are also involved in other conversions which result in 9,9-diphenylbifluorenyl in 38%



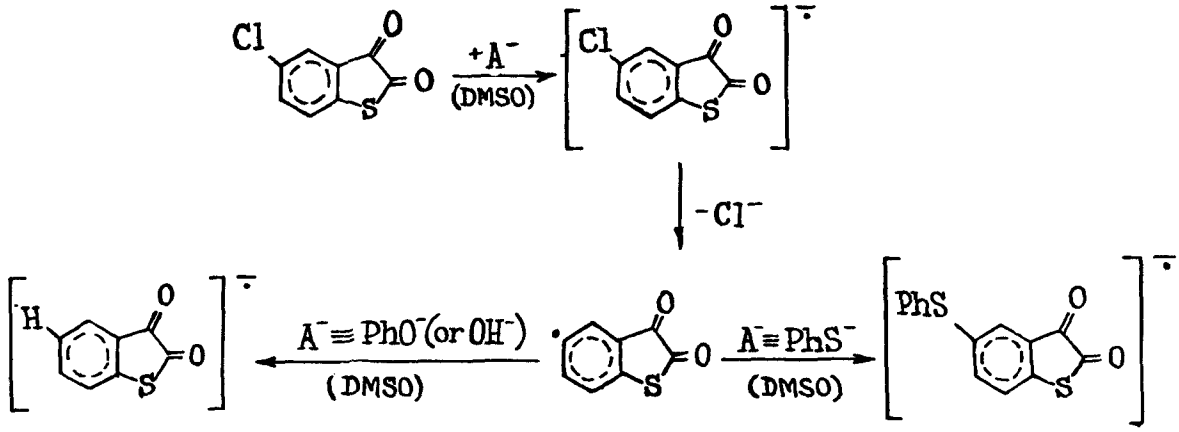
X= Cl , NO_2 , N_3 , $C_6H_5SO_2$, OAr



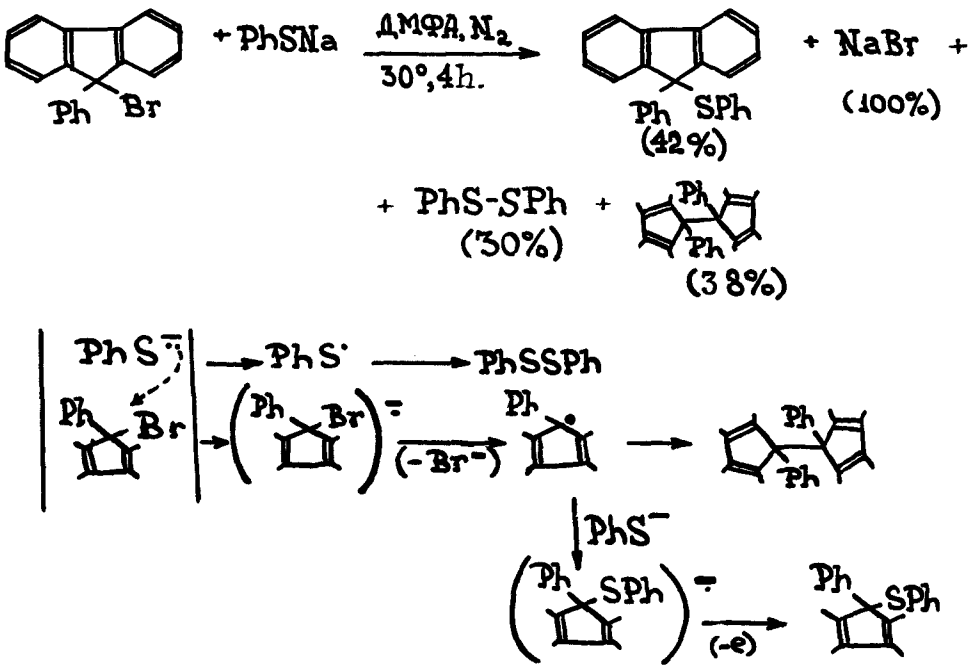




Scheme 4



Scheme 5



Scheme 6

yield and diphenyldisulfide in 30% yield. The formation of these unexpected substances is at variance with the usual picture of nucleophilic substitution. Special attention should be devoted to the fact that radical traps such as oxygen or tetrabromobenzoquinone inhibit the formation of both the unexpected compounds and the thioarylation product. Consequently, the stage of electron transfer from the nucleophile to substrate lies on the main pathway of the reaction. This stage produces the phenylthiyl radical and the anion radical of the initial substrate. Both the radical products are involved in further conversions: the phenylthiyl radical yields diphenylsulfide while the substrate anion radical-9-fluorenyl radical. The latter reacts by two pathways. It couples to give bifluorenyl (isolated) while by reacting with the nucleophile it forms the anion radical of, so to say, the nucleophilic substitution product. Further propagation of the chain proceeds via

transfer of the electron of this anion radical to an unreacted substrate molecule which then loses the bromine atom, thereafter reacts with the nucleophile, and so on.

The mechanism shown in Scheme 6 differs from conventional S_N1 or S_N2 mechanisms just by the presence of the one-electron redox stage. The driving force for this stage is probably a facile elimination of the bromine atom to give the fluorenyl radical with a free valency at the 9 position adjoining the three benzene nuclei which all stabilize the radical center.

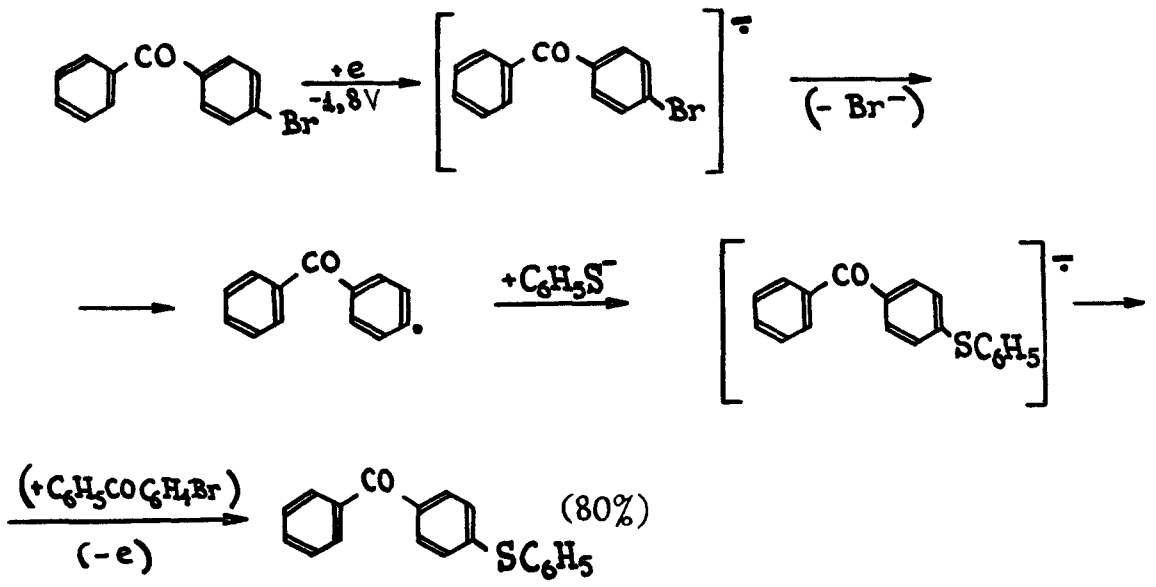
3 THE PUSHING OF SUBSTITUTION REACTIONS INVOLVING ORGANOSULFUR COMPOUNDS

These reactions can be pushed by creating conditions which favor primary formation of anion radicals. For this purpose, both electrochemical and purely chemical inducements can be employed.

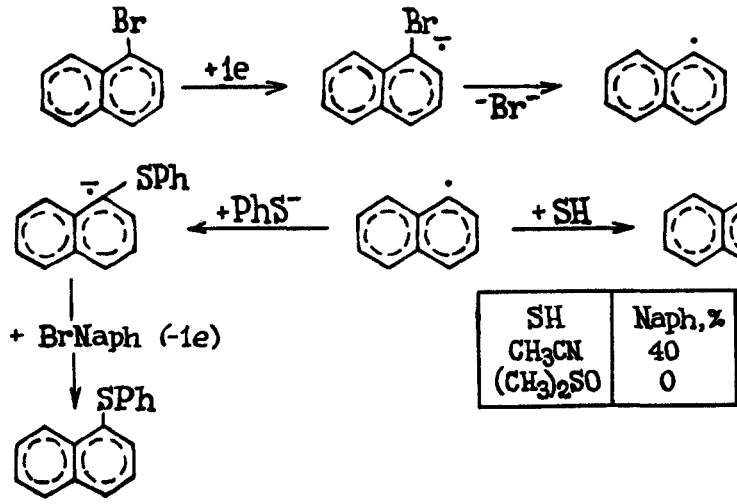
3.1 Electrochemical Inducement

Let us consider two examples where thioarylation is facilitated electrochemically. The first example is provided by Ref. 14. Nucleophilic substitution of bromine by the thiophenolate ion in 4-bromobenzophenone necessitates quite hard conditions. On applying potentials, the substitution proceeds readily to give high yields (80%). It is therefore sufficient to apply a potential that provides merely formation of the substrate anion radical (the potentials and consumption of electricity were strictly controlled in Ref. 14. Thereafter a chemical reaction in the bulk of the solution occurs to give 4-phenylthiobenzophenone (Scheme 7).

The second example follows.[15] 1-Bromonaphthalene does not react with thiophenolate at all. If, however, through a solution containing 1-bromonaphthalene, the tetrabutylammonium salt of thiophenol and dimethylsulfoxide (DMSO) one passes an electric current the formation of 1-phenylthionaphthalene in 100% yield is observed even at room temperature. This requires a potential corresponding to the initial current of the wave of reduction of bromonaphthalene to the 1-napththyl radical. Of interest here is the difference in consumption of electricity: in the absence of thiophenolate, bromonaphthalene is reduced consuming two electrons per molecule, whilst in the presence of thiophenolate the substitution product is formed quantitatively consuming two electrons for as many as ten bromonaphthalene molecules. The reaction with the thiophenolate ion is catalytic in the sense of consumption of current and involves the following stages (see Scheme 8):



Scheme 7



SH	Naph,%	PhS-Naph,%
CH_3CN	40	32
$(CH_3)_2SO$	0	100

Scheme 8

— Formation of the 1-bromonaphthalene anion radical which rapidly converts to the 1-naphthyl radical.

— Interaction of the naphthyl radicals with thiophenolate. The process occurs in the vicinity of the electrode and competes to yield unsubstituted naphthalene at the expense of the reaction of the radicals with solvent molecules (in Scheme 8 the solvent is designated as SH).

— Oxidation of the anion radicals of the product by neutral substrate molecules, occurring in the bulk of the solution.

— The continuation of the chain, comprising destruction of the 1-bromonaphthalene anion radicals.

Aside from bromonaphthalene, as a substrate, use can be made of bromobenzophenone (see Scheme 6) or bromobenzonitrile,[15] i.e. compounds containing not only bromine but also other electrochemically active groups. As a substituting fragment, one may incorporate not only the thiophenyl but thiomethyl or thiotertbutyl groups. The substitution products are obtained in high yields (from 60 to 95%), with one electron consumed per as many as 20 to 30 substrate molecules. The reactions occur at room temperature but without applying potentials they do not proceed at all.

The electrochemical method for pushing synthesis of organo-sulfur compounds is characterized by the following important advantages:

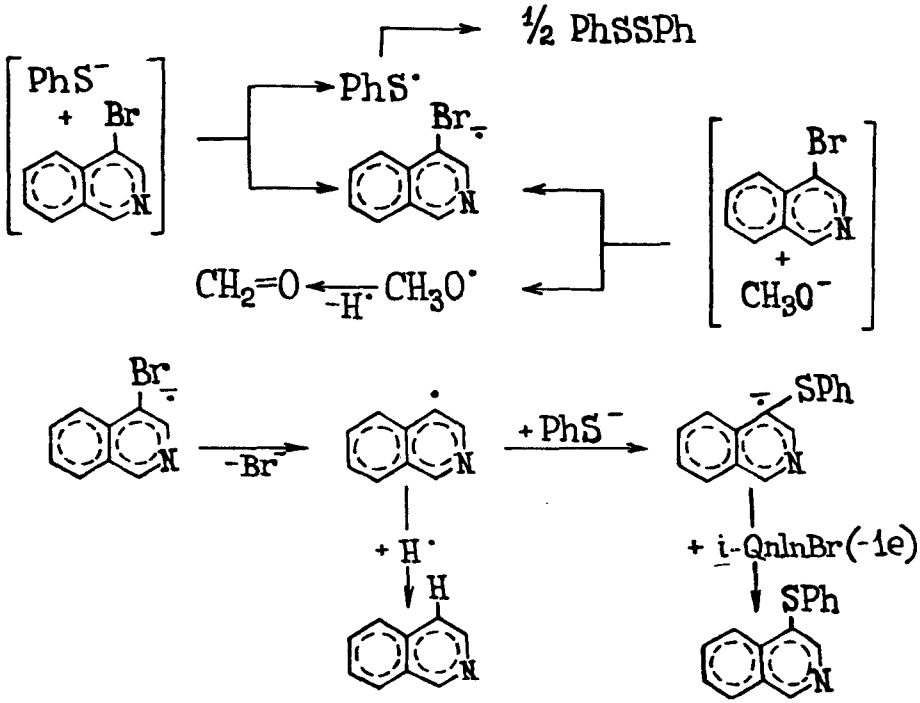
— The reactions are selective, proceed with rather high yields, and necessitate no activation of the substrate by introducing electron acceptor substituents.

— The starting halogen derivatives possess higher electron affinity than the sulfur-containing products. This offers facile transfer of the excess electron from the anion radical of the product to the substrate. The conditions for a chain reaction are thereby created, and the process becomes catalytic from the viewpoint of yield in current.

— An electrode potential can be applied initiating substitution of the starting molecules without the final substitution product being reduced.

— The undesirable hydrogen addition at the free valency site of the σ-radical due to reaction with solvent can be suppressed. To accomplish this, a solvent should be taken having a sufficient dissociating capacity but insufficient capacity to eliminate the hydrogen atom.

Thus, if the electrochemically induced reaction of 1-bromonaphthalene with $PhSNBu_4$ is carried out in acetonitrile, approximately equal quantities of naphthalene and 1-phenylthionaphthalene will be formed. If the same reaction is conducted in dimethylsulfoxide, phenylthionaphthalene will be formed in 100% yield whilst naphthalene will not be formed at all. Such an effect of the compared solvents on the reaction result agrees with literature data[16,17] which suggest that the capacity to give off a hydrogen atom is much lesser for sulfoxide than for acetonitrile.



Scheme 9

3.2 *Chemical Inducement*

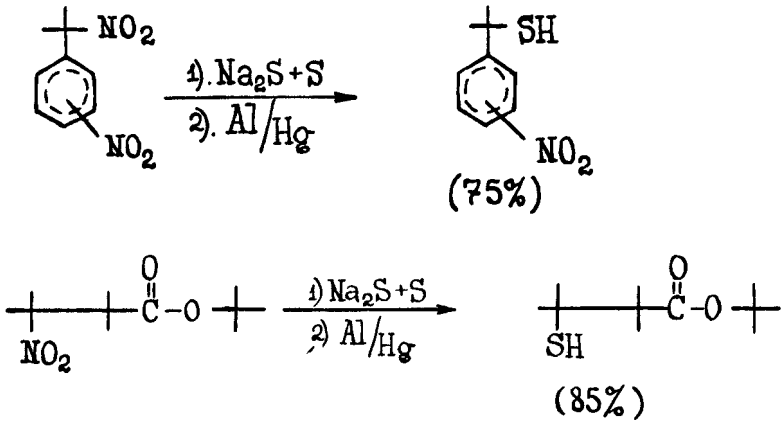
Three papers should be noted when considering purely chemical ways to exert influence on the course of reactions involving the electron transfer stages and comprising introduction of sulfur-containing groups.

The first[18] proposes to use sodium methylate to accelerate thioarylation of 4-bromoisoquinoline with sodium thiophenolate. Introduction of sodium methylate provides, along with thiophenolate, one more source of the electron needed for generating the substrate anion radical. However, while the thiophenolate converts to the phenylthiyl radical, then to diphenyldisulfide and is thus removed from the reaction sphere, in the presence of the methylate ion the generation of the substrate anion radicals occurs with conservation of a much greater portion of thiophenolate. In the presence of sodium methylate the total rate of thioarylation rises and the yield of 4-phenylthioisoquinoline increases. Addition of azobenzene suppresses the action of sodium methylate. All the foregoing is summarized in Scheme 9.

It is noteworthy that the presence of sodium methylate stimulates the formation of just 4-phenylthioisoquinoline, whereas the product of competing substitution, 4-methoxyisoquinoline, is formed only in trace quantities. Under the action of the methylate ion, however, a portion of the isoquinolyl σ-radicals converts to unsubstituted isoquinoline, to yield simultaneously formaldehide.

The second paper[19] is concerned with a method for direct conversion of nitrocompounds to thiols. The method involves the treatment of nitrocompounds in DMSO with a mixture of sodium sulfide and sulfur, followed by reduction with aluminium amalgam (Scheme 10).

Let us consider the first stage of the synthesis—the interaction of a nitrocompound with sodium sulfide. The sodium sulfide alone is not very effective—the reactions proceed slowly to give low yields. The addition of elemental sulfur markedly speeds up the conversions and increases the yields to 75–85%. The stimulating effect of elemental sulfur is easy to explain in terms of a radical chain mechanism that has convincingly been borne out in many reactions of aliphatic nitrocompounds.[7] According to this mechanism the reaction starts with one-electron transfer from the nucleophile to the nitrocompound. Further conversions are typical of the $S_{RN}1$ mechanism (Scheme 11).



Scheme 10

$$R_3C\text{-}NO_2 + {}^{-}S\text{-}S_X^{-} \longrightarrow R_3C\text{-}NO_2^{\cdot-} + {}^{\cdot}S\text{-}S_X^{-};$$

$$R_3C\text{-}NO_2^{\cdot-} \longrightarrow R_3C^{\cdot} + NO_2^{-};$$

$$R_3C^{\cdot} + {}^{-}S\text{-}S_X^{-} \longrightarrow R_3C\text{-}\dot{S}\text{-}S_X^{-};$$

$$R_3C\text{-}\dot{S}\text{-}S_X^{-} + R_3C\text{-}NO_2 \longrightarrow$$

$$\longrightarrow R_3C\text{-}NO_2^{\cdot-} + R_3C\text{-}S\text{-}S_X^{-};$$

$$R_3C\text{-}S\text{-}S_X^{-} \longrightarrow R_3C\text{-}S^{-} + S_X$$

Scheme 11

It can be supposed that the donor activity of the nucleophile, the sulfide ion, increases on distribution of the negative charge over the polysulfide chain of the ion appearing on the addition of elemental sulfur to sodium sulfide. Such distribution enhances electron mobility and the electron transfer is facilitated. That is why the reaction in hand can be stimulated by so simple a method, by merely adding elemental sulfur.

The interaction of a nitrocompound with a thionucleophile can be forced to take an entirely new course resulting in substitution of nitro group by hydrogen. For this aim, one should employ the methylthoilate ion as a sulfur-containing nucleophile.[20] The first stages of the reaction are completely identical. They involve generation of the anion radical of the initial nitrocompound which eliminate the nitro group to yield a carboradical (Scheme 12a). The latter abstracts a hydrogen atom from the methylthiolate to yield the denitration product as shown in Scheme 12a. Carboradicals with an aryl substituent in α or β positions are essentially stabilized due to conjugation[20] and behave as less active hydrogen acceptors. That is why the interaction between such radicals and methylthiolate ion yields not only the denitration product, but also the anion radicals of the corresponding methylthioether. These aryl-containing anion radicals exhibit delocalisation of spin density in aromatic nucleus, which facilitates electron transfer from methylthioether anion radical to the initial nitrocompound to favor the chain process. As a consequence these aryl-containing nitrocompounds, when reacting with methylthiolate, may yield the products of the substitution of the nitro group by the thiomethyl fragment.[20] The prominent feature of Scheme 12a is a high ability of the nitrocompound anion radical to eliminate the nitrite ion as a leaving group. In the treatment[21] this property was used as a basis for a conventional method for preparing aryl substituted olefins from nitroparaffins. When reacting with aromatic carbonyl or imine compounds, nitroparaffins can transform to nitroarylolefins. Nitro groups of nitroarylolefins can replace by hydrogens on a simple addition of thiophenole and sodium sulfide in dimethylformamide, Scheme 12b. The authors believe[21] that the reaction involves simultaneous additions of thiophenol to the olefinic bond and of an electron to the nitro group. So, the reaction is initiated by the anion radical of the addition product. $R'R''C(SPh(CH)R''')NO_2^{-}$. The resulting arylolefin is formed on elimination of the nitrite ion and phenylthioradical. The latter in its turn gives diphenyldisulfide. The yields of the desired arylolefins are high and attain 80–90%.[21]

Finally, the third work[22] deals with directed influence on anisylation of the thianthrene cation

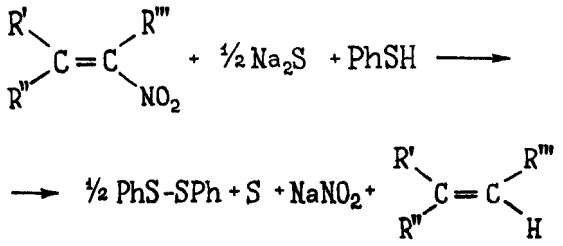
$$R_3CNO_2 + CH_3S^- \longrightarrow R_3CNO_2^{\cdot-} + CH_3S^{\cdot};$$

$$R_3CNO_2^{\cdot-} \longrightarrow R_3C^{\cdot} + NO_2^-;$$

$$R_3C^{\cdot} + H_3CS^- \longrightarrow R_3C\text{-}H + H_2\dot{C}S^-;$$

$$H_2\dot{C}S^- + R_3CNO_2 \longrightarrow H_2C{=}S + R_3CNO_2^{\cdot-}$$

Scheme 12a



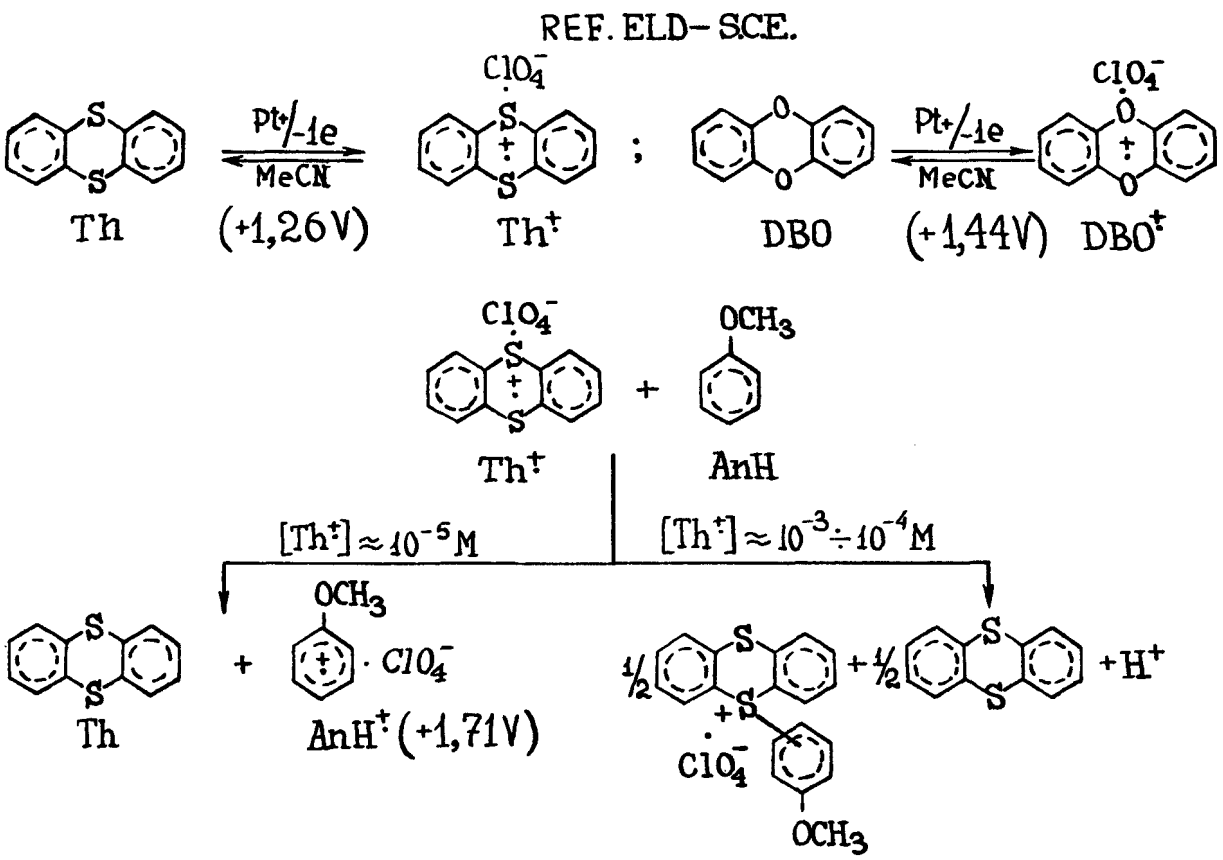
Scheme 12b

radical. This process results in the sulfonium salt of thianthrene (the anion being ClO_4^-) in 90% yield. Also, a side reaction takes place involving the one-electron reduction of the thianthrene cation radical with anisole. As to the main substitution reaction, it is accelerated by a factor of 200 by introducing the dibenzdioxane cation radical. Note that this cation radical is formed at more positive potentials than does the thianthrenyl one, and is consequently more active as an oxidant.

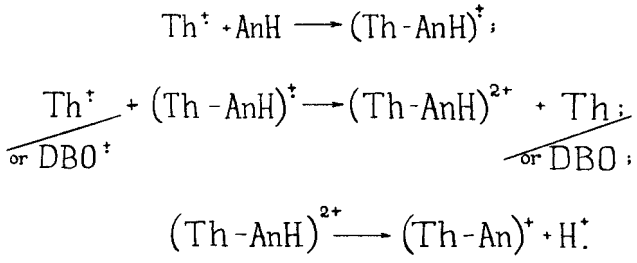
Decreasing the concentration of the initial thianthrenyl radical from $10^{-3} \div 10^{-4}$ M to 10^{-5} M changes the reaction result: the sulfonium salt is not formed at all and there proceeds the one-electron transfer alone to afford uncharged thianthrene and the anisole cation radical (Scheme 13).

A kinetic study[22] has revealed that anisylation of the thianthrene cation radical involves the following elementary stages (Scheme 14):

— Formation of the complex of the thianthrene cation radical with anisole.



Scheme 13



Scheme 14

— Oxidation of the cation radical complex to a dication complex. This stage is the key one and controls reaction rate.

— Rapid deprotonation of the dication complex to give the final product, the sulfonium salt.

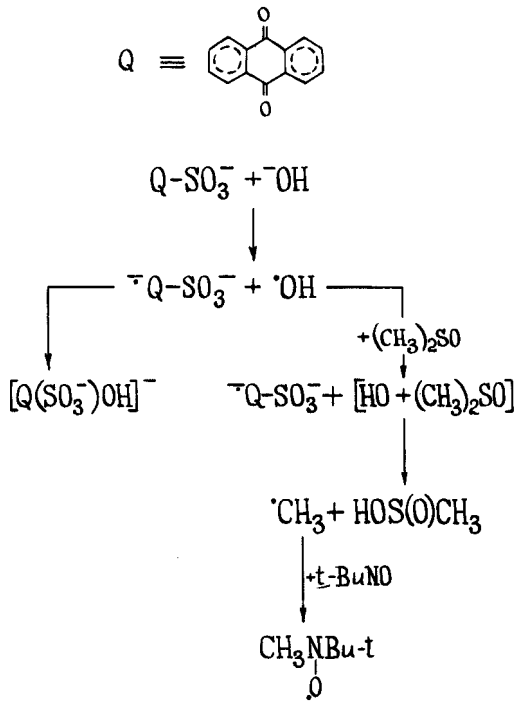
Since the reaction is led by the dication complex $(Th\text{-}AnH)^{2+}$ the final result should depend on the stationary concentration of this complex. The methods of regulating the process are therefore apparent:

— To increase the stationary concentration of the complex $(Th\text{-}AnH)^{2+}$, a stronger oxidant, compared to the thianthrene cation radical, should be introduced. The dibenzdioxane cation radical is such an oxidant. The presence of the latter increases the reaction rate by two orders of magnitude.

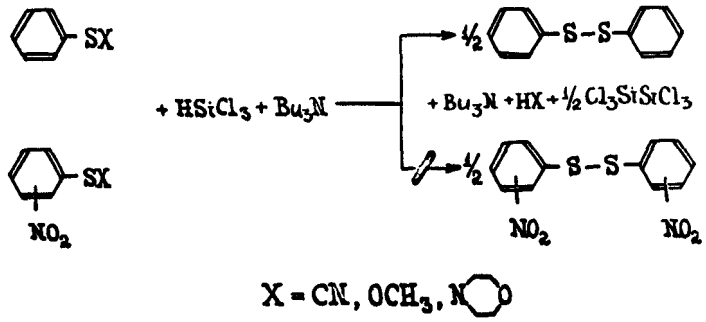
— To decrease the stationary concentration of the complex $(Th\text{-}AnH)^{2+}$, it is sufficient to decrease the concentration of the thianthrene cation radical being here both an oxidant and a substrate. In this case the equilibrium concentration of the cation radical complex $(Th\text{-}AnH)^{+}$ decreases as well. The rate of anisylation (the main process) sharply drops. As this takes place, the rate of the side process—one-electron transfer from anisole to the thianthrene cation radical—does not decrease so drastically. And it is this sole process that occurs.

4 THE ROLE OF SOLVENT IN DEVELOPMENT OF ION RADICAL PROCESSES

When considering the nature of the solvent as a means of directed influence on the course of substitution reactions of organo-sulfur compounds, one should take into account the solvent role just at the radical stage, provided the latter is involved in the reaction mechanism. The same dimethylsulfoxide plays a different role in different reactions. Reaction 8 enhances the stability of the intermediate so that attack by the phenylthiolate ion can take place. The dimethylsulfoxide can also completely inhibit the substitution, as it has been observed for hydroxylation of anthraquinone sulfonic acids[23] (Scheme 15). Hydroxylation of these sulfonic acids begins only at high temperatures and attains an appreciable rate at 180 to 200°. The authors[23] adduce arguments following which the substitution proceeds by a latent radical pathway without outgoing of the major portion of quinone anion radicals into the bulk of the solution (Scheme 15). The amount of the anion radicals, detectable by the E.P.R. method, does not exceed 10% and after a while their concentration becomes independent of reaction duration. Introduction of inhibitors such as oxygen or potassium ferricyanide prevents the anion radical formation while the yield of oxyanthraquinone even somewhat rises. This implies that the substrate anion radicals are produced in a side process. The introduction of inhibitors increases the rate of formation of the final product due to regeneration of uncharged substrate molecules, occurring on oxidation of the anion radicals. A substantial portion of substrate molecules undergoes hydroxylation by a pathway



Scheme 15



Scheme 16

not involving the outgoing of the intermediate particles from the solvent cage. The final products are oxyanthraquinones. With dimethylsulfoxide, as solvent, the complex of the OH· radicals with DMSO molecules is formed and the reaction proceeds by a pathway associated with outgoing of the sulfoanthraquinone anion radicals into the bulk of the solution. This facilitates the first stage; the anion radicals of the starting anthraquinone sulfonic acid are formed even at 25° and their accumulation is completed in several hours.[24,25] Thereafter, however, no further development of the reaction is observed and no substitution of the sulfonic groups by hydroxyl ones occurs—the hydroxyl radicals are irreversibly bound with DMSO (Scheme 15). The formation of free CH_3 radicals from DMSO, shown in Scheme 15, has been borne out by the radical trap method.[24]

5 THE METHODS OF DIRECTED INFLUENCE, BASED ON VARIATION OF THE DEGREE OF IONIC COUPLING IN ELECTRON TRANSFER PRODUCTS

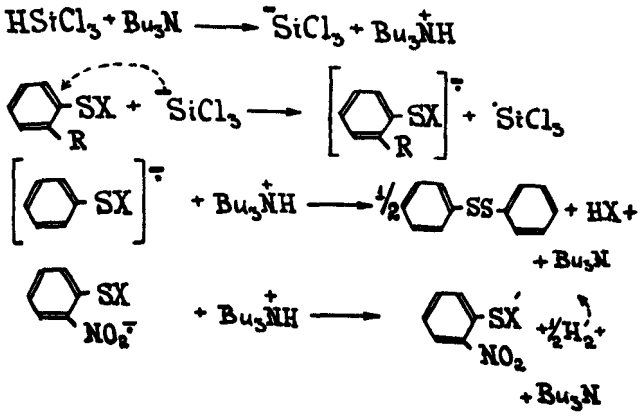
Two striking examples of such influence are found in our studies.

5.1 Redox Interaction Between the Components of an Ion Radical Salt and the Problem of Removing Nitrosulfenate Protection

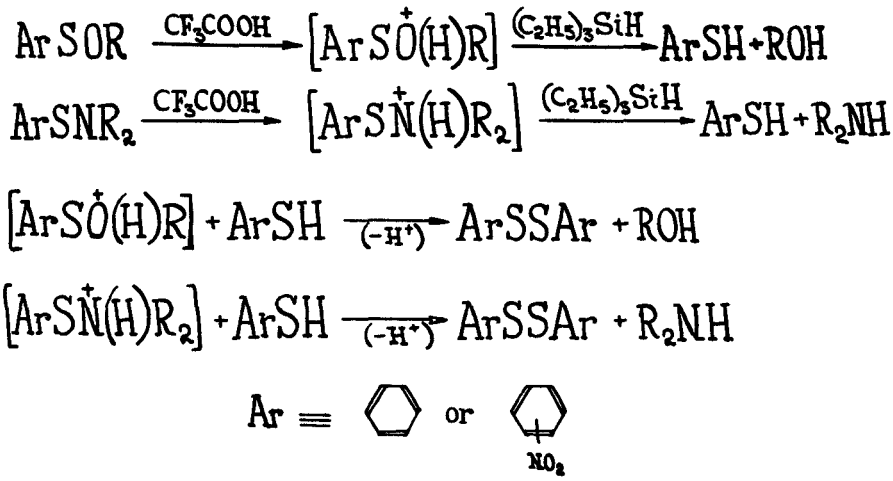
The proper choice of conditions needed for removing nitrosulfenate protection can be made starting from properties of nitroarylsulfenate anion radicals. The introduction of nitroartlsulfenate protection is used in various conversions of complicated (particularly, bioorganic) molecules containing amino or oxy groups. To recover activity of the amino or oxy groups after these conversions the nitroarylsulfenate protection is to be removed. The competition of acceptor fragments should therefore be taken into account for a sulfur-containing rather than nitro group to be reduced. Among a number of reductive systems the trichlorosilane-tributylamine system has been investigated.[3] It has been found that by using trichlorosilane and tributylamine, only those arylsulfene derivatives can be reduced which contain no nitro groups. Nitroarylsulfenate analogues remain unchanged in these conditions (Scheme 16).

Introduction of nitrosulfene compounds into a mixture of trichlorosilane and tributylamine results in hydrogen evolution.

Trichlorosilane with tributyl amine yields the trichlorosilyl anion and tributylammonium cation. From this stage, a chain of conversions begins, involving one-electron transfer from the trichlorosilyl anion to sulfene molecule. Nitrobenzenesulfene compounds produce stable anion radicals which give off an electron to the proton present in the counterion—the tributylammonium cation (Scheme 17).



Scheme 17



Scheme 18

The sulfur-containing group in the nitrobenzenesulfene compounds is not cleaved. In this they are markedly different from the benzenesulfenic analogues not containing nitro groups. Due to the presence of a nitro group in the nucleus, one-electron oxidation of the anion radical with a proton, followed by hydrogen evolution, occurs instead of the cleavage of the sulfur-containing fragment.

From the foregoing, it is clear that for reactions beginning from the anion radical formation stage the deciding factor is the change in distribution of the unpaired electron, caused by the nitro group, a powerful acceptor substituent. The nitro group captures the unpaired electron thus preventing the reductive cleavage of the SOR and SNR_2 groups.

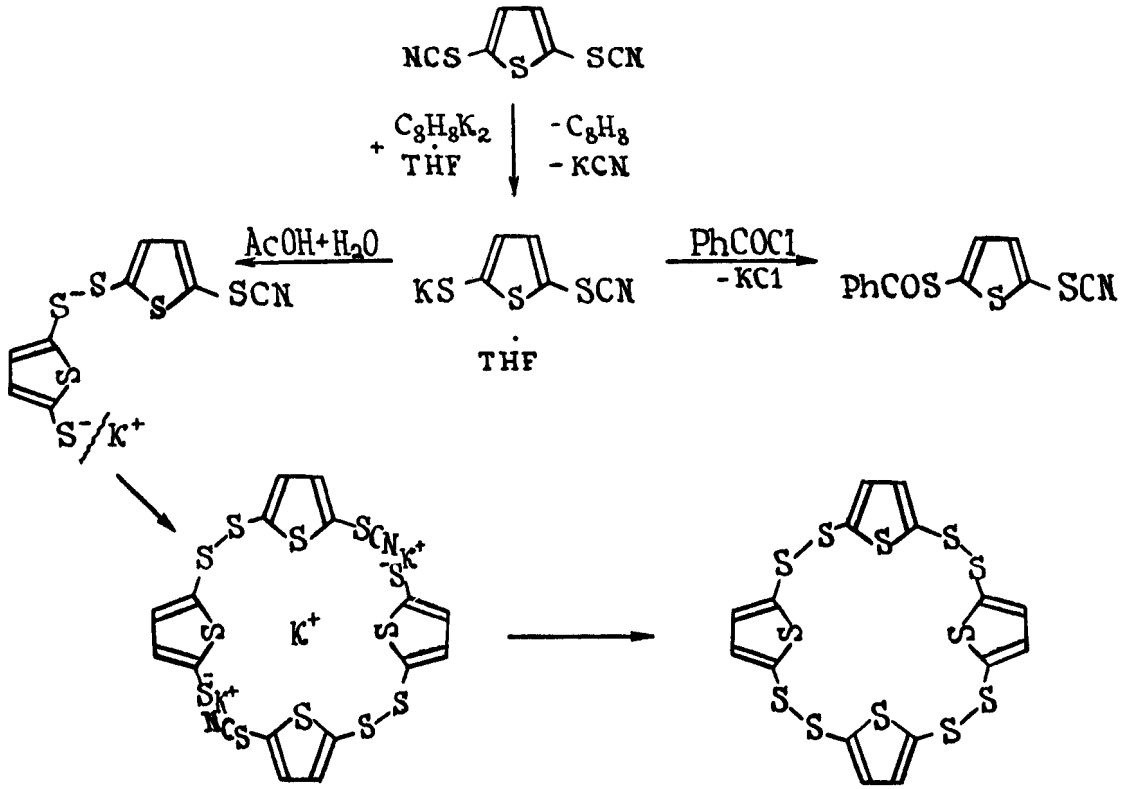
The predisposition of groups such as SOR to reductive cleavage sharply increases after their protonation. For the trifluoroacetic acid—triethylsilane system the reduction has been found to proceed selectively to afford dinitrodiphenyldisulfides in high yields. The reaction is described in Scheme 18 that is applicable to both nitrated and non-nitrated analogues.[3]

5.2 *Coordination Interactions in the Salt-like Product of Electron Transfer and the Problem of Template Synthesis*

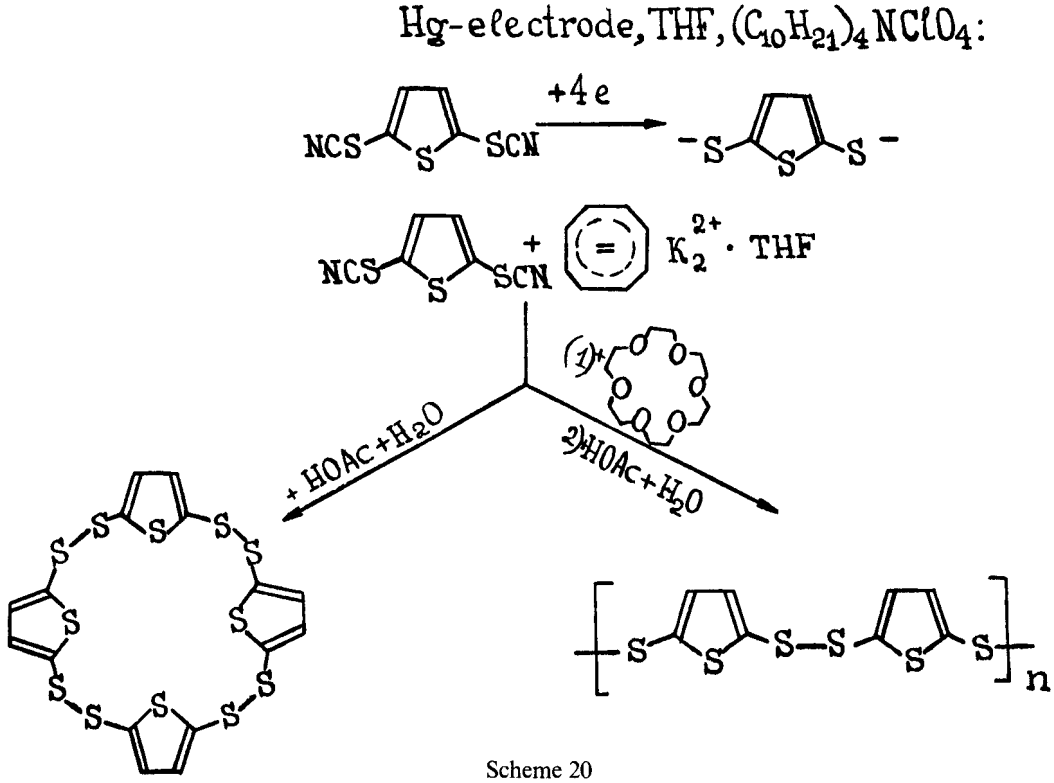
In Refs. 26, 27 a directed synthesis of cyclic poly(thienylene-2,5-disulfide) has been reported (Scheme 19). A 2,5-dithiocyanothiophene molecule contains two thiocynanide groups, which allows to reduce one of them to the mercaptide group and to direct further conversions along the way of interaction of the mercaptide with thiocyanide groups. This interaction may be either inter- or intramolecular one. The presence of the sulfur atom in the thiophenic nucleus might supposedly lend the predisposition toward coordination with the potassium cation to the product of partial reduction. This provides a means for producing a template to assemble the anionoid fragments to give a cyclic product. As has been established by our studies[26,27] the reaction of equimolecular quantities of 2,5-dithiocyanothiophene and cyclooctatetraenedipotassium in tetrahydrofuran results in potassium 5-thiocyano-2-thienylmercaptide, potassium cyanide and cyclooctatetraene. Thiocyanothienylmercaptide is stable in THF and has been identified through its monobenzoyl derivative. On addition of aqueous acetic acid into THF, dissociation of the thienlmercaptide pair with the potassium cation occurs and poly(disulfide) is formed. The polysulfide has a cyclic structure, as established by X-ray diffraction experiment.[27] The cyclization proceeds, most likely, via intermediate formation of disulfides according to Scheme 19.

The metal cation coordinates the anionoid fragments, allowing them to couple to one another within the matrix. This probably occurs in the course of homogeneous reduction. The correlation between the diameter of the cavity of the multithiaheterocycle obtained and the doubled radius of the potassium cation provides support for this view.

On electrode reduction performed in the same solvent (THF) the cleavage of both the thiocyanic



Scheme 19



Scheme 20

groups of 2,5-dithiocyanothiophene is observed within a single four-electron wave (Scheme 20).

The results of the homogeneous and electrode reactions can be brought closer together by introducing 2,5-dithiocyanothiophene into interaction with cyclooctatetraenedipotassium in the presence of crown-18-ether-6. The ether binds the potassium cation thus guiding the condensation to formation of a linear rather than cyclic product. In the presence of the crown ether the principal product proves to be poly(disulfide) of the linear type (Scheme 20).

Thus, the coordination with a metal cation can crucially alter the direction of further conversion of an electron transfer product.

In summary, the significance of the electron transfer stage in various reactions of organo-sulfur compounds has been demonstrated. The methods have been analyzed allowing one to exert influence on these reactions. The fruitfulness of the idea of electron transfer for purposes of organosulfur synthesis has thereby been illustrated.

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