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Advances in the chemistry of sulphenic acid amides

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ABSTRACT. Results of recent investigations in the area of sulphenic acid amides have been systematised and correlated in the review. Reactions of sulphenamides occurring with the generation of anions, radicals and nitrenes have been considered, as well as reactions accompanied by fussion of the S–N bond and oxidation of the sulphur atom.

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I. Introduction

The chemistry of sulphenic acid amides began in 1911 with the discovery by Zincke of sulphenic acid chlorides and the study of their reactions with nitrogen-containing compounds.[1] The rapid development of this area of hetero-organic chemistry is explained primarily by the useful properties of representative compounds of this class, which are widely used as pesticides,[2] vulcanising agents,[3] electrolytic additives[4,5] and other valuable reagents used in industry and agriculture. The high lability of the S–N bond in sulphenamides, and also the presence of two centres for reaction (sulphur and nitrogen) make sulphenic acid amides extremely valuable as reagents for the synthesis of sulphides,[6,7] disulphides,[8–11] trisulphides,[12] new types of suphenamides,[13] sulphenic acid esters,[14] sulphinamides[15] and sulphonamides.[16]

The interest displayed in sulphenic acid amides by any investigators caused at one time the appearance of a series of reviews[17–22] which reflected in some degree the progress in the chemistry of sulphenamides in a particular period. In the present review results of recent investigations in the chemistry of sulphenic acid amides are systematised and correlated. In particular, reactions are considered which occur with fission of the N–H bond and generation of anions, radicals and nitrenes and reactions accompanied by fission of the S–N bond and oxidation of the sulphur atom.

II. Reactions occurring with fission of the N–H bond

1. Generation of N-anions

Dissociation of N-substituted sulphenamides containing electron-acceptor groups at the sulphur and nitrogen atoms in polar organic solvents leads to the formation of N-anions of the sulphenamides in the stabilisation of which the sulphur atom and the electron acceptor groups participate:[23–25]

$$RSNHR^1 \rightleftharpoons \overset{\ominus}{R}SNR^1 + H^{\oplus},$$
$$\overset{\ominus}{R}SNR^1 \leftrightarrow \overset{\ominus}{R}S{=}NR^1.$$

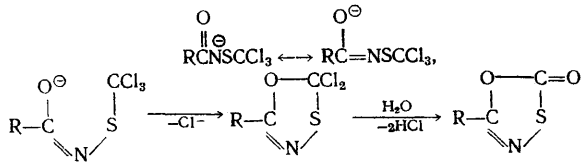
Table 1. pK_a values of N-substituted sulphenamides[25] $RSNHR^1$.

R	R^1	pK_a	Method of determination
C_6H_5	$C_6H_5SO_2$	11.87	a
4-$CH_3C_6H_4$	$C_6H_5SO_2$	12.66	a
4-ClC_6H_4	$C_6H_5SO_2$	10.80	a
4-$NO_2C_6H_4$	$C_6H_5SO_2$	8.20	a
2-$NO_2C_6H_4$	$C_6H_5SO_2$	8.45	a
2,4-$(NO_2)_2C_6H_3$	$C_6H_5SO_2$	5.76	a
2,4-$(NO_2)_2C_6H_3$	4-$CH_3OC_6H_4SO_2$	6.08	a
2,4-$(NO_2)_2C_6H_3$	4-$CH_3C_6H_4SO_2$	5.98	a
2,4-$(NO_2)_2C_6H_3$	4-$ClC_6H_4SO_2$	5.33	a
2,4-$(NO_2)_2C_6H_3$	4-$BrC_6H_4SO_2$	5.31	a
2,4-$(NO_2)_2C_6H_3$	3-$NO_2C_6H_4SO_2$	4.62	a
2,4,6-$(NO_2)_3C_6H_2$	$C_6H_5SO_2$	2.69	a
2,4,6-$(NO_2)_3C_6H_2$	4-$CH_3C_6H_4SO_2$	2.90	a
2,4,6-$(NO_2)_3C_6H_2$	4-$ClC_6H_4SO_2$	2.44	a
3,4,5-$(NO_2)_3C_6H_2$	4-$ClC_6H_4SO_2$	2.88	a
C_6H_5	C_6H_5CO	12.30	a
4-$NO_2C_6H_4$	C_6H_5CO	9.60	a
2-$NO_2C_6H_4$	C_6H_5CO	10.40	a
4-$NO_2C_6H_4$	CH_3CO	10.78	a
2-$NO_2C_6H_4$	CH_3CO	11.38	a
2,4-$(NO_2)_2C_6H_3$	CH_3CO	9.67	a
CCl_3	C_6H_5CO	7.64	b
CCl_3	4-$CH_3C_6H_4CO$	7.67	b
CCl_3	4-$CH_3OC_6H_4CO$	7.69	b

Note. a, potentiometric titration in 50% acetone; b, indicator buffer-free method in acetone.

The stability of the N-anions formed in the dissociation process was determined by the pK_a of sulphenamides (Table 1) the magnitude of which varied over a wide range depending on sulphenamide structure.

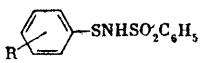
Anions of N-acyltrichloromethanesulphenamides are converted in the presence of base into 5-aryl-1,3,4-oxathiazol-2-ones,[24] which limits the choice of method for determining the pK_a of these compounds.



From a comparison of the pK_a values of N-acyltrichloromethanesulphenamides and the pK_a of dichloroacetic acid (2.70) determined by the same method,[24] it may be concluded that the anions of N-acyltrichloromethanesulphenamides possess high stability.

The character of the substituent on the arenesulphenyl group of N-arenesulphonylarenesulphenamides exerts a greater influence on the stability of the N-anion than does the character of a substituent on the arenesulphonyl group. This is linked with the greater ability of divalent sulphur in comparison with hexavalent sulphur to transmit the inductive influence of the substituent. This situation is also confirmed by correlation analysis, specifically by a comparison of the reaction constants ρ_1 and ρ_2 obtained from the correlation relationships between the pK_a values of two series of N-arenesulphonylarenesulphenamides and the Hammett σ constants (Tables 2, 3).

Table 2. Correlation parameters of a reaction series of N-benzenesulphonylarenesulphenamides.[25]

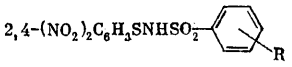


R	pK_a	σ	ρ_1	r
4-NO_2	8.20	0.232	4.717	0.999
4-Cl	10.80	0.227		
H	11.87	0.000		
4-CH_3	12.86	−0.170		

The maximum in the 380–420 nm region in the electronic spectra of solutions of N-arenesulphonylarenesulphenamides corresponds to the absorption of N-anions and is absent from the spectra of N-arenesulphonylalkylarenesulphenamides. An increase in absorption maximum was observed with increase in the acidic properties of N-arenesulphonylarenesulphenamides and also with increase in solvent polarity.[25]

The generation of anions from N-acyl- and N-arenesulphonylarenesulphenamides may be affected by the action on them of alkali or alcoholates.[25] The stability of the resulting sodium salts is caused by the acidic properties of sulphenamides. The sodium salts of N-arenesulphonylnitrobenzenesulphenamides are converted during a few minutes in air to a dark wine-red resin dissolving readily in water with the formation of dark red solutions. The sodium salts of N-arenesulphonyldinitrobenzenesulphenamides are more stable towards the action of moisture and remain unchanged for an extended time.

Table 3. Correlation parameters of a reaction series of N-arenesulphonyl-2,4-dinitrobenzenesulphenamides.[25]



R	pK_a	σ	ρ_2	r
3-NO_2	4.62	0.710	1.537	0.997
4-Br	5.31	0.232		
4-Cl	5.33	0.227		
H	5.76	0.000		
4-CH_3	5.98	−0.170		
4-CH_3O	6.08	−0.268		

In alcoholic solution the sodium salts of N-arenesulphonylarenesulphenamides are methylated at the nitrogen atom by methyl iodide with the formaiton of N-arenesulphonylmethylarenesulphenamides.

2. Generation of N-radicals

Homolysis of the N–H bond in sulphenamides by the action of oxidising agents was noticed for the first time by Lecher and co-workers.[26] They established that under the action of PbO_2 on bis-(benzenesulphenyl)imide in an inert organic solvent the bis-(benzenesulphenyl)imine radical is formed in the stabilisation of which the sulphur atom participates:

$$\cdot\,\mathrm{PhS\!-\!N\!-\!SPh} \leftrightarrow \mathrm{PhS{=}N\!-\!SPh} \leftrightarrow \mathrm{PhS\!-\!N{=}SPh}$$

The action of PbO_2 or (tert.-BuO)$_2$ on N-arenesulphenamides in an inert organic solvent leads to the generation of N-arenesulphenylarylaminyl radicals Ar–SN–Ar^1 (Ar is Ph, 2-$NO_2C_6H_4$, 4-ClC_6H_3; Ar^1 is $MeOC_6H_4$, 4-$(Me)_2(NC_6H_4)$, having as a rule a red colour.[18,26–28]

It was established by EPR[29] that radicals RSNS(Ar) = NSR, coloured blue, green or brown depending on the structure of R and Ar, are formed on oxidation of sulphenamides RSNHC(Ar) = NSR with lead dioxide or silver oxide in diethyl ether in the presence of potassium carbonate.

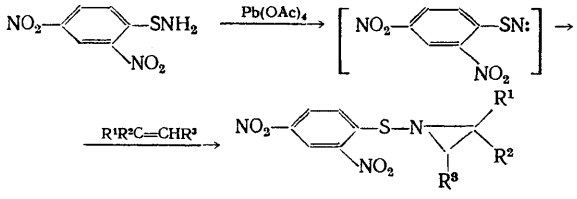
The formation of N-arenesulphenylacylaminyl radicals has been observed[30–33] on heating N-arylsulphenyl-N,N′-bis-(acyl)-arenesulphinamidines in inert organic solvents (benzene, toluene, etc.).

$$\mathrm{ArS(=NAc)N(SAr)Ac} \overset{70\text{–}80^\circ\mathrm{C}}{\rightleftharpoons} 2\mathrm{ArS\dot{N}Ac},$$
$$\mathrm{Ac} = \mathrm{ArSO_2},\ \mathrm{ArCO}.$$

At 120–140 °C the homolysis became irreversible.

3. Generation of nitrenes

The oxidation of 2,4-dinitrobenzenesulphenamide with lead tetraacetate in aprotic organic solvents leads to 2,4-dinitrobenzenesulphenylnitrene which forms the corresponding aziridines with olefins:[34–36]



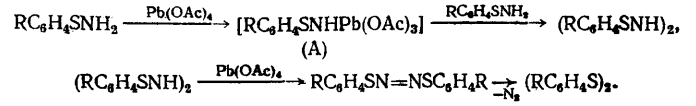
The capture of 2,4-dinitrobenzenesulphenylnitrene by olefins and not by the sulfenamide as in the case of sulphides[37] is explained by the fact that the 2,4-dinitrophenyl group reduces the electron density at the sulphur atom as a result of which the sulphur atom is not capable of undergoing electrophilic attack by 2,4-dinitrobenzenesulphenylnitrene.

In the absence of olefins the oxidation of 2,4-dinitrobenzenesulphenamide by lead tetraacetate leads to N-(2,4-dinitrophenyl)-2,4,dinitrobenzenesulphenamide, which in the opinion of the authors[35] is formed by attack of the nitrene at the nitrogen or sulphur atoms of 2,4-dinitrobenzenesulphenamide. The formation of N,N′-di-[2,4,6-tri-(tert.-butyl)benzene]diiminosulphur in the reaction of 2,4,6-tri-(tert.-butyl)benzenesulphenamide with lead tetraacetate,[38] is also explained by attack of the nitrene at the sulphur atom of the sulphenylamide.

Oxidation of 2,4-dinitrobenzenesulphenamide with lead tetraacetate in the presence of (*Z*)-phenylpropene[34,36] leads to a mixture of trans- and cis-1-(2,4-dinitrobenzenesulphenyl)-2-methyl-3-phenylaziridines, the ratio of which depends on the type of solvent used, the ratio of reactants, and also the order of mixing the reagents. In benzene the ratio of trans- and cis-isomers is 1 : 1, but in chloroform and in methylene chloride it is 3 : 1. In more polar solvents (CH_3CN, CH_3OH) the overall yield of both isomers is reduced. On introducing lead tetraacetate into a mixture of 2,4-dinitrobenzenesulphenamide and (*Z*)-phenylpropene, together with aziridine the formation is observed of N-(2,4-dinitrophenyl)-2,4-dinitrobenzenesulphenamide and partial isomerisation of (*Z*)-phenylpropene into (*E*)-phenylpropene, while addition of a mixture of 2,4-dinitrobenzenesulphenamide and lead tetraacetate in chloroform to (*Z*)-phenylpropene leads to the formation in high yield of only aziridine.

It has been assumed[34] that triplet nitrene is formed initially in the oxidation. This is in equilibrium with singlet nitrene and they both react with (*Z*)-phenylpropane. Since sulphides are effective traps for singlet nitrenes[39] then introduction of sulphide $4\text{-}ClC_6H_4.SCH_2CH=CH_2$ into the reaction mixture changes both the overall yield of aziridines and the ratio of isomers. At the same time in the presence of effective trapping agents for triplet nitrenes PhC(R) = CH_2 (R = Ph, Me) the ratio of cis- and trans-isomers is unchanged although the overall yield of aziridines is reduced.

When sulphenamides $RC_6H_4SNH_2$ (R = 2-NO_2, 4-NO_2, 4-Cl) are oxidised with lead tetraacetate in the presence of olefins the corresponding disulphides are isolated. These are formed as a result of the following conversions:[40]



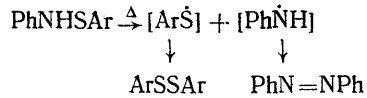
The formation of the nitrenoid intermediate (A) was confirmed by the fact that on oxidation of 4-nitrobenzenesulphenamide with lead tetraacetate in DMSO, N-4-nitrobenzenesulphenyldimethylsulphoximide was obtained.[40]

III. Reactions proceeding with fission of the S–N bond

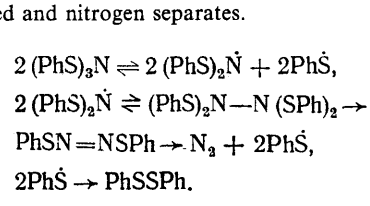
In contrast to the sulphur–nitrogen bond in sulphonamides, which is very stable, the S–N bond in sulphenamides is labile and is readily split by nucleophilic and electrophilic reagents. This was even mentioned by Zincke and co-workers[41] when studying the reaction of naphthalenesulphenyl chlorides with naphthylamines. The stability of S–N bonds in sulphenamides towards nucleophilic and electrophilic reagents is in direct relationship to their bond energies on which there are no data in the literature. This gap is compensated to some extent by data on the order of the S–N bond and force constants. From a study of the vibrational spectra of sulphenamides it was established that the bond order of S–N in N-methyl- and N,N-dimethylsulphenamides is greater than unity,[3] but the force constants of the stretching vibrations of this bond in bis-(arenesulphenyl)imides, N-acyl- and N-arenesulphonylarenesulphenamides are $1894.7-2024.9 \times 10^{-17}$ J.mol.m^2.[42]

1. Homolytic fission of the S–N bond

Homolytic fission of the S–N bond of sulphenamides is as a rule observed on heating or on UV irradiation. For example heating N-phenylarenesulphenamides to 195 °C[43] leads to the formation of the corresponding disulphides and azobenzene which is explained by homolysis of the S–N bond and subsequent dimerisation of the resulting radicals:



The thermal stability of sulphenamides is reduced with increase in their basicity, which occurs in the presence of electron donating substituents bound to the sulphur and nitrogen atoms.[44] Thus homolysis of the S–N bond in tribenzenesulphenamide[45] occurs on mild heating or on UV irradiation. In this case the disulphide is formed and nitrogen separates.



The ease of homolysis of the S–N bond in the given case is explained by the increased stability of the dibenzenesulphenylaminyl radical in the stabilisation of which the sulphur atom participates. In support of this case tristrifluoromethanesulphenylamide is also inclined to photolyse.[46]

$$(CF_3S)_3N + (CF_3S)_2NMe \xrightarrow{h\nu} (CF_3S)_2NH + CF_3SSCF_3 + \\ + (CF_3S)_2NCH_2NHSCF_3.$$

Stable free radicals RSNC(Ar) = NSR are formed on photolysis of sulphenamides $(RS_2)NC(Ar) = NSR$ in aprotic organic solvents.[29] It is not excluded that thermal rearrangement of sulphenamides $4\text{-}RC_6H_4N(R^1)SC = CR^2$ with the formation of derivatives of indole[47] is also effected after homolysis of the S–N bond.

2. Heterolytic fission of the S–N bond

Heterolysis of the S–N bond in sulphenamides occurs under the action of both electrophilic and nucleophilic reagents which are frequently used for synthetic purposes. The reactions of sulphenamides with hydrogen halides, carboxylic and sulphonic acid chlorides and with isocyanates have been well studied and proceed according to the general scheme.[3]

$$RSNHR^1 + X^{\delta+} - Y^{\delta-} \rightarrow \left[RS\overset{\oplus}{N}(X)HR^1 - Y^{\ominus} \right] \rightarrow RSY + R^1NHX,$$

$$XY = HCl,\ TsCl,\ AcCl,\ PhNCO.$$

Nucleophilic substitution at the sulphur atom of the amide group is also widely used in various syntheses. Thus reactions of sulphenamides with dialkyl phosphites,[48] thiols,[49] thiocarboxylic acids,[50] and compounds containing active methylene groups[51] are used for obtaining O,O′-dialkyl 5-alkyl phosphonothionates, disulphides, bis-(acyl)disulphides and sulphides:

$$R^1SN(R^2)R^3 + NuH \rightarrow R^1SNu + R^2(R^3)NH,$$
$$NuH = (RO)_2POH,\ RSH,\ RCOSH,\ (NC)_2CH_2,\ (RCO)_2CH_2.$$

When sulphenamides interact with thiol esters of sulphonic acids[52,53] a trans-sulphenylation of the sulphenamide occurs:

$$R^1SN(R^2)R^3 + R^4SO_2SR^5 \rightarrow R^5SN(R^2)R^3 + R^4SO_2SR^1.$$

The reaction is irreversible and takes place only on the interaction of highly nucleophilic sulphenamides (R^2 and R^3 are electron-donating groups) with highly reactive thiol esters of sulphonic acids (R^4 is an electron-accepting group).

Heterolysis of the two S–N bonds in trisulphenamides on interaction with trivalent phosphorus and arsenic compounds leads to the formation of the corresponding imides and disulphides:[54,55]

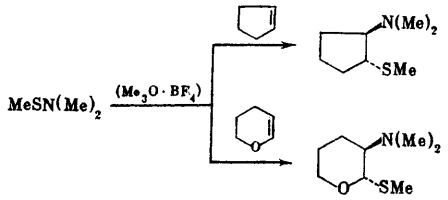
$$Ph_3E + \underset{\displaystyle R}{\overset{|}{S}}-N(SR)_2 \rightarrow Ph_3\overset{\oplus}{E}-\underset{\displaystyle R}{\overset{|}{S}}\overset{\ominus}{N}(SR)_2 \rightleftharpoons Ph_3E\begin{matrix}SR\\ \diagdown N(SR)_2\end{matrix} \rightarrow$$

$$\rightarrow Ph_3E{=}NSR + RSSR,$$

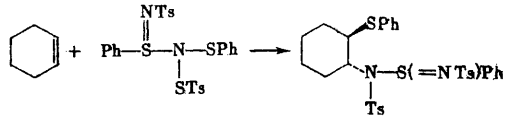
$$R = Ph,\ CF_3;\quad E = P,\ As.$$

At the same time the interaction of *p*-nitrobenzenesulphenamide with triphenylphosphine under the conditions of the Appel reaction proceeds anomalously with splitting of the S–N bond and the formation of the ylide $(p\text{-}NO_2C_6H_4S)_2C{=}P(Ph)_3$.[56]

Heterolytic fission of the S–N bond in the presence of olefins is accompanied by addition of the resulting fragments to the C=C bond of the olefin. For example, heterolytic fission of the S–N bond of N-(dimethyl)methanesulphenamide in nitromethane in the presence of cyclopentene or 3,4-dihydro-2H-pyran leads to the formation of trans-1-dimethylamino-2-methylthiocyclopentane or trans-2-dimethyl-amino-3-methylthiotetrahydropyran.[57,58]

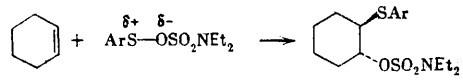


The addition of sulphenamides $PhSNR^1R^2$ [$R^1 + R^2 = (CH)_4$, $R^1 + R^2 = (CH_2)_2O(CH_2)_2$, $R^1 = H$, R^2 = t.-Bu] to the C=C bond of cyclohexene, octene and indene[59,60] also occurs predominantly at the trans-position. Strong proton acids or Lewis acids are catalysts of the aminosulphenylation of olefins. Under conditions of acid catalysis N-benzenesulphenyl-N,N′-bis-(p-toluenesulphonyl)benzenesulphinamidine adds to the C=C bond of cyclohexene with the formation of a benzosulphinamidine trisubstituted at the nitrogen atom.[61]

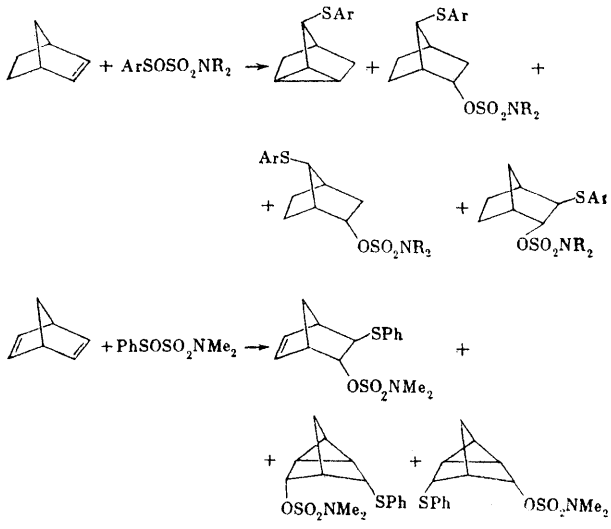


The reactivity of sulphenamides towards olefins in the heterolytic addition reaction increases with an increase in the electrophilicity of the sulphur atom which may be achieved by inserting SO_3 in the S–N bond of sulphenamides.[62] Using this procedure Zefirov and co-workers[63] carried out for the first time the sulphamatosulphenylation of olefins which comprises the interaction of sulphenamides with SO_3 in an inert solvent at a reduced temperature of −85 °C, with subsequent addition of the insertion products to the C=C bond of olefins. The sulphamatosulphenylation of cyclohexene is stereospecific and leads to the trans-1,2-adduct:

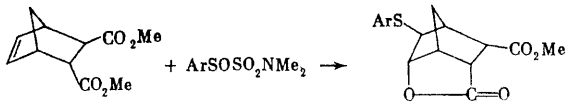
$$ArSNEt_2 + SO_3 \xrightarrow[-\,80^\circ C]{CH_2Cl_2} ArSOSO_2NEt_2$$



The sulphamatosulphenylation of norbornene and norbornadiene[63] is accompanied by rearrangement of the carbon skeleton which finally leads to a mixture of several products:



On sulfamatosulphenylation of bicyclo[2.2.1]hept-2-en-endo-cis-5,6-dicarboxylic acid dimethyl ester cyclisation of the adducts occurs with the formation of arylthiolactones:[63]



The use of pyridine/sulphur trioxide as SO_3 donor[64] makes it possible to carry out this reaction at room temperature. It was shown[65] that the sulphamate group is relatively easily replaced both by weak (CF_3COO^-, $HCOO^-$) and by strong (Br^-) nucleophiles.

IV. Reactions occurring with oxidation of the sulphur atom

Oxidation reactions of the divalent sulphur in sulphenamide to the quadri- and hexavalent state forming sulphin- and sulphonamides have been known and studied for a long time. However a series of reactions has been carried out during which the sulphur in sulphenamides increases its valency by two units and adds an atom of halogen or an imino, alkoxy or amido group. These reactions have become known relatively recently and have still not been studied fully.

1. Oxidative imination of sulphenamides

Conversions accompanied by oxidation of an element and by addition of an imino group are taken to be called oxidative imination reactions.[66]

It has been established[67] that sulphenamides $ArSNRR^1$ (R = H, Alk; R^1 = Alk) react with the sodiochloroamides of arenesulphonic acids according to the general reaction scheme of oxidative imination with the formation of N,N′-substituted amides of iminosulphinic acids:

$$ArSNRR^1 + TsNNaCl \xrightarrow{-NaCl} ArS(=NTs)NRR^1.$$

Sulphenamides ArSNHX [X = C(=NH)NH_2, C(=NH)Alk, C(=NH)SAlk, C(=NH)OAlk] are iminated by sodiochloroamides of sulphonic acids,[67] N-chlorobenzamide,[68] and N-bromobenzamidine.[69] N-Acylsulphenamides p-$NO_2C_6H_4SNHAc$ are iminated in the presence of base by N-chloroacet- and N-chlorobenzamide[70] and also by N-bromobenzamidine.[68] However attempts[67] to effect the imination of N-acyl- and N-arenesulphonylarenesulphenamides with the sodiochloroamides of sulphonic acids in acetone were completed without a result which is explained by the reduced electron density at the sulphur atom of these sulphenamides.

The mechanism of oxidative imination of sulphenamides by N-halogen compounds has not been investigated in detail, however by analogy with the oxidative imination of sulphides[71,72] it has been proposed[73] that the chlorine atom of the N-halogen compound attacks electrophilically the sulphur atom of the sulphenamide with the formation of a chlorosulphonium intermediate which forms an ion pair with the amidate anion:

$$ArSNRR^1 + ClNHR^2 \rightleftharpoons \left[Ar\overset{\oplus}{S}(Cl)NRR^1\overset{\ominus}{N}HR^2 \right] \xrightarrow{-HCl} ArS(=NR^2)NRR^1.$$

The possibility of forming the chlorosulphonium intermediate by electron transfer from the sulphur atom to the positively charged chlorine atom is not excluded.[74] It is evident that the electron density on the sulphur atom must be sufficient for electrophilic attack by chlorine cations. In this connection it seemed of interest to activate the sulphur atom in the oxidative imination reaction by creating an α-N-anionic centre[75] which makes possible the imination of N-substituted sulphenamides containing electron accepting groups on the sulphur and nitrogen atoms. Thus the selection of conditions for imination in the case of N-monosubstituted sulphenamides is determined by their acidic properties.[25] Unionised sulphenamides with $pK_a > 11$[74–76] are iminated in acetone by sodiochloroamides of sulphonic acids:

$$RSNHR^1 + ArSO_2NNaCl \xrightarrow{-NaCl} RS(=NSO_2Ar)NHR^1,$$

R=Ph, 2-$NO_2C_6H_4$, 4-$NO_2C_6H_4$, R^1=H;
R=CH_2Cl, R^1=AlkCO, ArCO; R=Ph, R^1=AlkCO, ArCO; R=Ph, 4-MeC_6H_4, R^1=$ArSO_2$.

Sulphenamides with pK_a 8–11[77,78] are not iminated in acetone but are iminated in strongly basic solvents of high dielectric constant (aqueous alkaline solution, pyridine, etc.) capable of dissociating sulphenamides with the formation of an α-N-anionic centre:

$$RSNHR^1 \rightleftharpoons RS\overset{\ominus}{N}R^1 + H^{\oplus},$$
$$RS\overset{\ominus}{N}R^1 \leftrightarrow RS^{\ominus} = NR^1.$$

The sodium salts of such sulphenamides are readily iminated by sodiochloramides of sulphonic acids in acetone.

$$\left[RS{-}\overset{\cdots}{N}R^1 \right]^{\ominus}Na^{\oplus} + ArSO_2NNaCl \xrightarrow{-NaCl} \left[ArSO_2N{-}\overset{R}{S}{-}NR^1 \right]^{\ominus}Na^{\oplus}$$

R=4-$NO_2C_6H_4$, R^1=AlkCO, ArCO
R=4-ClC_6H_4, 2-NOC_6H_4, 4-$NO_2C_6H_4$, R^1=$ArSO_2$.

Sulphenamides with $pK_a < 8$[79–82] are iminated in acetone and also in aqueous alkaline medium and in pyridine since the concentration of N-anion is still sufficiently high, however they are not iminated in benzene, toluene, hexane or in solvents of low dielectric constant suppressing the dissociation of the sulphenamide.

$$\left[RS{=}NR^1\right]^{\ominus}H^{\oplus} + ArSO_2NNaCl \xrightarrow[-NaCl]{} \left[ArSO_2N{=}\underset{\underset{R}{|}}{S}{=}NR^1\right]^{\ominus}Na^{\oplus}$$

R=EtOCOCCl$_2$, R^1=ArCO, R=CCl$_3$, R^1=AlkCO, ArCO, ArSO$_2$; R=CFCl$_2$, R^1=AlkCO, ArCO; R=CF$_2$Cl, R^1=AlkCO, ArCO.

Since the formation of sodium salts of sulphenamides occurs first on interacting sulphenamides having $pK_a < 6$ with sodiochloroamides of sulphonic acids (N-chlorobenzenesulphonamide has pK_a 9.5[83]), their imination was conducted at a reactant ratio of 1:2.[25,80]

$$RSNHSO_2R^1 + ArSO_2NNaCl \xrightarrow[-\left[ArSO_2NHCl\right]]{} \left[RS{=}NSO_2R^1\right]^{\ominus}Na^{\oplus} \xrightarrow{ArSO_2NNaCl} \rightarrow \left[ArSO_2N{=}\underset{\underset{R}{|}}{S}{=}NSO_2R^1\right]^{\ominus}Na^{\oplus}$$

R = 2,4-(NO$_2$)$_2$C$_6$H$_3$, CCl$_3$

The direction of the reaction of N-acyl-p-nitrobenzenesulphenylamides with the sodiochloroamide of sulphonic acids depends on the conditions. Imination of these sulphenamides is effected in aqueous alkaline medium but in pyridine the interaction of these compounds is accompanied by fission of the S–N bond and the formation of symmetrical N,N′-bis-(arenesulphonyl)-p-nitrobenzenesulphinamidines.[78] A similar symmetrisation was also observed[24] in the interaction of N-acylmethanesulphenamides with sodiochloroamides of sulphonic acids in acetone.

$$MeSNHCOR + ArSO_2NNaCl\cdot xH_2O \rightarrow \begin{cases} \rightarrow MeS(=NSO_2Ar)NHCOR \\ \rightarrow MeS(=NSO_2Ar)NHSO_2Ar \end{cases}$$

This process has been studied in more detail in the example of the reaction of sodiochloroamides of sulphonic acids with bis-(arenesulphenyl)imides, the products of which were a mixture of N,N′-bis-(arenesulphonyl)arenesulphinamidines and N-arenesulphonylarenesulphinamidines.[84]

$$ArSNHSAr + 3PhSO_2NNaCl\cdot xH_2O \rightarrow \begin{cases} \rightarrow ArS(=NSO_2Ph)NH_2 \\ \rightarrow Ar(=NSO_2Ph)NHSO_2Ph \end{cases}$$

Ar = 2-NO$_2$C$_6$H$_4$, 4-NO$_2$C$_6$H$_4$.

The formation of a mixture of two products is explained by two factors. The first is the low rate of imination of sulphenamides which is determined by the low electron density on the sulphur atom and the impossibility of compensating for it by the formation of an α-N-anionic centre since bis-(arenesulphenyl)imides are relatively weak NH-acids with pK_a 10.8.[84] The second is the lability of the sulphur–nitrogen bond, and its fission in the presence of water of crystallisation with the formation of diaryldisulphides and arenesulphenamides, the further imination of which leads to the formation of the reaction products.

$$ArSNHSAr \rightarrow \begin{cases} \rightarrow ArSNH_2 \\ \rightarrow [ArSOH] \rightarrow 0.4ArSSAr + 0.2ArSO_3H + 0.4H_2O \end{cases}$$

$$ArSNH_2 + PhSO_2NNaCl \rightarrow ArS(=NSO_2Ph)NH_2,$$

$$0.4ArSSAr + PhSO_2NNaCl \rightarrow 0.8ArS(=NSO_2Ph)NHSO_2Ph.$$

Such ideas were confirmed on studying the reaction of bis-(2,4-dinitrobenzenesulphenyl)imide with the sodiochloroamide of benzenesulphonic acid in acetone where the formation of N-benzenesulphonyl-2,4-dinitrobenzenesulphinamidine and of 2,4,2′,4′-tetranitrodiphenyldisulphide was observed. These, as is known[85], are not imidated by the sodiochloroamides of sulphonic acids:

$$[2.4\text{-}(NO_2)_2C_6H_3S]_2NH \xrightarrow{PhSO_2NNaCl\cdot xH_2O} \begin{cases} \rightarrow 2.4\text{-}(NO_2)_2C_6H_3S(=NSO_2Ph)NH_2 \\ \rightarrow [2.4\text{-}(NO_2)_2C_6H_3S-]_2 \end{cases}$$

The imination of N-acyl- and N-arenesulphonylsulphenamides by N-chloroamides of carboxylic acids[68,86] is carried out in the presence of organic bases which play the role not only of acceptors of hydrogen chloride but also are capable of dissociating the initial sulphenamides:

$$\left[RS{=}NAc\right]^{\ominus}H^{\oplus} + R^1CONHCl \xrightarrow[-HCl]{} \left[R^1CON{=}\underset{\underset{R}{|}}{S}{=}NAc\right]^{\ominus}H^{\oplus}$$

2. Oxidative halogenation of sulphenamides

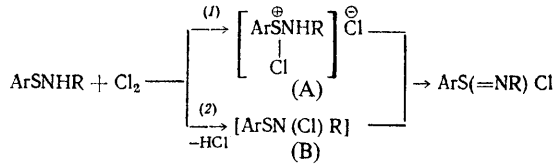
The chlorination of N-substituted sulphenamides by chlorine in non-aqueous aprotic organic solvents leads to the formation of the acid chlorides of N-substituted iminosulphinic acids.[87]

$$ArSNHR + Cl_2 \xrightarrow[-HCl]{} ArS(=NR)Cl,$$

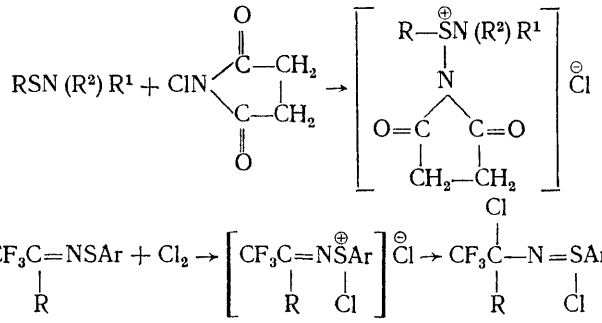
R=ArSO$_2$, ArCO, tert-Bu.

Dichloroamides of sulphonic acids, N-chloroimides, and tert.-butyl hypochlorite are also used as chlorinating agents. The chlorination of weakly nucleophilic sulphenamides is carried out in the presence of organic bases. The susceptibility of sulphenamides to oxidative chlorination is explained by the electron density on the sulphur atom. The presence of electron accepting groups on the sulphur and nitrogen atoms hinders oxidative chlorination or makes it impossible.[87]

The mechanism of the oxidative chlorination of sulphenamides has not been studied in detail. However allowing for the possibility of attack of chlorine cations at both the sulphur atom and the nitrogen atom it has been proposed[87] that the formation of the acid chlorides of iminosulphinic acids may occur by two concurrent schemes (1) and (2).



The most probable of these seems to be Scheme (1) since the intermediate N-chlorosulphenamides (B) [Scheme (2)] do not always succeed in rearranging to acid chlorides of iminosulphinic acids.[87] At the same time the appearance of chlorosulphonium salts of type (A) is recorded in reactions of N,N-dialkylsulphenamides with N-chlorosuccinimide,[88] and also of N-arylsulphenylketimines with chlorine:[89,90]



The hypothesis of a high probability of chlorinating sulphenamides at the sulphur atom is also in agreement with the principle of hard and soft acids and bases.[91] Evidently chlorination at the nitrogen atom is possible only in the event of low electron density at the sulphur atom, i.e. in the presence of strongly electron-accepting groups on the sulphur and nitrogen atoms. Replacement of a hydrogen atom on the nitrogen of N-arenesulphonylarene-sulphenamides by a metal atom increases the reactivity of the latter in oxidative chlorination reactions, which is seemingly explained by the increase in electron density at the sulphur atom as a result of the effects of the α-N-anionic centre:[92]

$$ArSN(Na)SO_2Ph + Cl_2 \rightarrow ArS(=NSO_2Ph)Cl + NaCl.$$

The oxidative chlorination of N,N-di(trifluoromethylsilyl)-trifluoro-methanesulphenamides is accompanied by splitting of the N–Si bond:[93]

$$CF_3SN(SiMe_3)_2 \xrightarrow[-ClSiMe_3]{Cl_2} [CF_3S(=NSiMe_3)Cl] \xrightarrow[-ClSiMe_3]{Cl_2} CF_3S(=NCl)Cl.$$

Only one sulphur atom participates in the oxidative chlorination of bis-(trifluoromethanesulphenyl)imide:[93]

$$(CF_3S)_2NH + Cl_2 \rightarrow CF_3S(=NSCF_3)Cl + HCl.$$

3. Oxidative alkoxylation and amidation of sulphenamides

The increased susceptibility of the sulphur atom of N-substituted sulphenamides to attack by chlorine cations under conditions of generating an α-N-anionic centre makes this method of activating sulphur promising in reactions accompanied by oxidation of the sulphur atom. For example, it has been shown[94] that the sodium salts of N-arenesulphonylarenesulphenamides are very readily chlorinated by tert.-butyl hypochlorite in alcohols (the reaction is exothermic) with the formation of alkyl esters of N-arene-sulphonylareneiminosulphinic acids (oxidative alkoxylation reaction).

$$ArSNHSO_2Ph + \text{tert-BuOCl} \xrightarrow{RONa} ArS(=NSO_2Ph)OR + \text{tert-BuOH} + NaCl,$$
$$R = Me, Et;\ Ar = 2\text{-}NO_2C_6H_4.$$

The chlorination of these salts by chlorine in acetone in the presence of dialkylamines[95] leads to the formation of N,N-dialkyl-N′-arenesulphonylarenesulphinamidines (oxidative amidation reaction).

$$ArSN(Na)SO_2Ph + Cl_2 + 2R_2NH \rightarrow ArS(=NSO_2Ph)NR_2 + NaCl + R_2NH\cdot HCl.$$

References

1. T Zincke *Ber.*, 1911, **44** 769
2. N N Mel'nikov, K V Novozhilov, T N Pylov *Khimicheskie Sredstva Zashchity Rastenii* (Chemical Agents for Plant Protection), Khimiya, Moscow, 1980, p. 287
3. D H R Barton, W D Ollis *Comprehensive Organic Chemistry* (Translated into Russian), Khimiya, Moscow, 1983, Vol. 5, p. 440
4. E E Kravtsov, R A Abakumenko, M M Kremlev, et al., Authors Certificate No. 295824 SSSR: *Byul. Izobret.*, 1971, (8) 78
5. A V Nikolaev, I V Koval', V A Aleksenko, M M Kremlev, *Authors Certificate No. 931345 SSSR: Byul. Izobret.*, 1982, (20) 43
6. T Kumamoto, S Kobayashi, T Mukaiyama *Bull. Chem. Soc. Jpn.*, 1972, **45**(3) 866
7. F A Davis *Int. J. Sulfur. Chem.*, 1973, **8** 71
8. K S Boustany, A B Sullivan *Tetrahedron Lett.*, 1970, **41** 3547
9. D N Harpp, T G Back *J. Org. Chem.*, 1971, **36** 3828
10. D A Armitage, M J Clark, C C Tso *J. Chem. Soc., Perkin Trans., 1*, 1972, (5) 680
11. M Masateru, K Tomonori, I E Kato, S M Kenji *Synthesis*, 1980, (9) 721
12. A B Sullivan, K Boustany *Internat. J. Sulfur. Chem. (A)*, 1971, **1** 207
13. H J Bestmann, W Stransky, O Vostrowsky *Chem. Ber.*, 1976, **109** 1694
14. D H R Barton, G Page, D A Widdowson *J. Chem. Soc. Chem. Comm.*, 1970, 1466
15. F A Davis, A J Friedmann, V K Nadir *J. Am. Chem. Soc.*, 1978, **100**(9) 2844
16. R S Glass, R Swedo *Synthesis*, 1977, (11) 798
17. N Kharasch, S J Potempa, H L Wehrmeister *Chem. Rev.*, 1946, **39**(42) 269
18. E Riesz *Bull. Soc. Chim. Fr.*, 1966, (4) 1449
19. C Hennart *Bull. Soc. Chim. Fr.*, 1967, (11) 4395
20. E Kuhle *Synthesis*, 1971, (12) 617
21. F A Davis, V K Nadir *Org. Prep. Proceed. Int.*, 1979, **11**(1) 33
22. Gaku Yamamoto *J. Jpn. Chem.*, 1978, **32**(3) 207
23. I V Koval', T G Oleinik, M M Kremlev *Zh. Org. Khim.*, 1981, **17** 665
24. I V Koval', A I Tarasenko, M M Kremlev, N P Molchanova *Zh. Org. Khim.*, 1981, **17** 533

25. I V Koval', T G Oleinik, A I Tarasenko, M M Kremlev *Zh. Org. Khim.*, 1985, **21** 2578
26. H Lecher, K Koeberle, P Stoecklin *Ber.*, 1925, **58** 423
27. S Hiroteru, M Koichi, M Takashi *Chem. Pharm. Bull. (Japan)*, 1979, **27**(10) 2316
28. L Benati, P C Montevecchi, P Spagnolo *J. Chem. Soc., Perkin Trans. 1*, 1982, (12) 3049
29. M Yozo, K Teruo, I Mamoru, K Masayoshi *J. Org. Chem.*, 1985, **50**(10) 1627
30. M M Kremlev, G F Kodachenko, S I Burmistrov, I V Koval', Authors Certificate No. 245771: *Byul. Izobret.*, 1969, (20) 16
31. M M Kremlev, I V Koval' *Zh. Org. Khim.*, 1970, **6** 1457
32. E S Levchenko, N P Pel'kis, V N Kalinina *Zh. Org. Khim.*, 1982, **18** 1191
33. E S Levchenko, N P Pel'kis, V N Kalinina *Zh. Org. Khim.*, 1982, **18** 1197
34. R S Atkinson, B D Judkins *J. Chem. Soc. Chem. Comm.*, 1979, (19) 833
35. R S Atkinson, B D Judkins *J. Chem. Soc., Perkin Trans., 1*, 1981, (9) 2615
36. R S Atkinson, B D Judkins, N Khan *J. Chem. Soc., Perkin Trans., 1*, 1982, (10) 2491
37. Y Hayashi, D Swern *J. Am. Chem. Soc.*, 1973, **95** 5205
38. R Mayer, D Decker, S Bleisch, G Domschke *J. Prakt. Chem.*, 1987, **329**(1) 81
39. W Ando, N Odigo, T Migita *Bull. Soc. Chem. Jpn.*, 1971, **44** 2278
40. T A Chaudri *Pak. J. Sci. Ind. Res.*, 1976, **19**(3) 115
41. T Zincke, K Eismayer *Ber.*, 1918, **51** 751
42. I V Koval', A I Tarasenko, M M Kremlev, R P Naumenko *Zh. Org. Khim.*, 1986, **22** 1178
43. F A Davis, C J Horner, E R Freetz, J F Stackhouse *J. Org. Chem.*, 1973, **38** 695
44. F A Davis *Int. J. Sulfur. Chem.*, 1973, **8** 71
45. D H R Barton, I A Blair, P D Magnus, R K Norris *J. Chem. Soc., Perkin Trans., 1*, 1973, 1031
46. H E Borowski, A Haas *Chem. Ber.*, 1982, **115** 523
47. J B Baudin, M Bekhazi, S A Julia, et al. *Synthesis*, 1985, (10) 56
48. S Torii, N Sayo, H Tanaka *Chem. Lett.*, 1980, (6) 695
49. L Benati, P C Montevecchi, P Spagnolo *Tetrahedron Lett.*, 1986, **27**(15) 1739
50. M Masateru, K Tomonori, I Eikoh, et al. *Synthesis*, 1980, (9) 721
51. J S Grosset, P K Dubey *J. Chem. Soc. Chem. Comm.*, 1982, 20) 1183
52. B G Boldyrev, T K Bilozor *Zh. Org. Khim.*, 1986, **22** 458
53. B G Boldyrev, T K Bilozor *Zh. Org. Khim.*, 1987, **23** 1878
54. J Almog, D H R Barton, P D Magnus, R K Norris *J. Chem. Soc. Perkin Trans., 1*, 1974, 853
55. A Haas, J Hahne *Z. Anorg. Allg. Chem.*, 1982, **490**(7) 230
56. I N Zhmurova, V G Yurchenko, A M Pinchuk *Zh. Obshch. Khim.*, 1985, **55** 321
57. R A Abramovitch, J Pilski *J. Chem. Soc. Chem. Comm.*, 1981, (14) 704
58. M C Caserio, J K Kim *J. Am. Chem. Soc.*, 1982, **104**(11) 3231
59. P Brownbridge *Tetrahedron Lett.*, 1984, **25**(34) 3759
60. L Benati, P C Montevecchi, P Spagnolo *Tetrahedron Lett.*, 1984, **25**(19) 2039
61. D H R Barton, M R Britten-Kelly, D Ferreira *J. Chem. Soc., Perkin Trans., 1*, 1978, **12** 1682
62. N S Zefirov, N V Zyk, A G Kutateladze, et al. *Zh. Org. Khim.*, 1986, **22** 24
63. N S Zefirov, N V Zyk, A G Kutateladze, Yu A Lapin *Zh. Org. Khim.*, 1987, **23** 392
64. N S Zefirov, N V Zyk, A G Kutateladze, Yu A Lapin *Zh. Org. Khim.*, 1987, **23** 229
65. N S Zefirov, N V Zyk, A G Kutateladze, et al. *Zh. Org. Khim.*, 1986, **22** 2462
66. E S Levchenko, A V Kirsanov *Uspekhi Khimiii Fosfororganicheskikh i Seraorganicheskikh Soedinenii* (Edited by A V Kirsanova) (Advances in the Chemistry of Organophosphorus and Organosulphur Compounds), Nauk. Dumka, Kiev, 1969, p. 261
67. J Goerdeler, B Redies *Chem. Ber.*, 1959, **92** 1
68. J Goerdeler, K Doerk *Chem. Ber.*, 1962, **95** 389
69. J Goerdeler, K Doerk *Chem. Ber.*, 1962, **95** 154
70. J Goerdeler, B Roose *Chem. Ber.*, 1962, **95** 394
71. K Tsujihara, N Furukawa, K Oae, S Oae *Bull. Chem. Soc. (Japan)*, 1969, **42** 2631
72. R Ruff, A Kucsmann *J. Chem. Soc., Perkin Trans., 2*, 1975, **2** 509
73. M M Campbell, G Johnson *Chem. Rev.*, 1978, **78**(1) 65
74. I V. Koval', T G Oleinik, M M Kremlev *Zh. Org. Khim.*, 1981, **17** 2174
75. I V Koval' *Voprosy Khimii i Khim. Tekhnologii* (Edited by M A Loshkareva) (Problems of Chemistry and Chemical Technology), Vishcha Shkola, Kharkov, 1980, **59** 58
76. I V Koval', A I Tarasenko, M M Kremlev *Zh. Org. Khim.*, 1978, **14** 111
77. I V Koval', T G Oleinik, M M Kremlev *Zh. Org. Khim.*, 1979, **15** 2319
78. I V Koval', T G Oleinik, M M Kremlev *Zh. Org. Khim.*, 1980, **16** 633
79. M M Kremlev, A I Tarasenko, V V Ryabenko, I V Koval' *Zh. Org. Khim.*, 1974, **10** 2320
80. M M Kremlev, S S Gontar' *Zh. Org. Khim.*, 1976, **12** 2001
81. I V Koval', A I Tarasenko, T G Oleinik, M M Kremlev *Zh. Org. Khim.*, 1979, **15** 1004
82. I V Koval', M M Kremlev, A I Tarasenko, Authors Certificate No. 450794 SSSR: *Byul. Izobret.*, 1974, (43) 56
83. J H Beale *J. Org. Chem.*, 1972, **37** 3871
84. I V Koval', A I Tarasenko, M M Kremlev, R P Naumenko *Zh. Org. Khim.*, 1986, **22** 1178
85. I V Koval', A I Tarasenko, M M Kremlev *Zh. Org. Khim.*, 1986, **22** 410
86. I V Koval', A I Tarasenko, I S Panchenko, N R Molchanova *Zh. Org. Khim.*, 1986, **22** 1712
87. L N Markovskii, T N Lubinina, E S Levcehnko, V V Pen'kovskii *Zh. Org. Khim.*, 1976, **12** 1049
88. M Haake, H Benack *Synthesis*, 1976, 308
89. Yu G Shermolovich, V S Talanov, G N Dolenko, L N Markovskii *Zh. Org. Khim.*, 1978, **14** 964
90. Yu G Shermolovich, V S Talanov, V V Pirozhenko, L N Markovskii *Zh. Org. Khim.*, 1982, **18** 2539
91. S Hauptmann, J Graefe, H Remane *Organic Chemistry* (Translated into Russian), Khimiya, Moscow, 1979, p. 831 [Original title "Lehrbuch der Organischen Chemie"]
92. I V Koval', A Yu Romanenko *Zh. Org. Khim.*, 1988, **24** 457
93. A Haas, R Walz *Chem. Ber.*, 1985, **118**(3) 3248
94. I V Koval' *Zh. Org. Khim.*, 1988, **24** 665
95. I V Koval', V D Zinukhov *Zh. Org. Khim.*, 1988, **24** 1784