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Nucleophilic Substitution in β-Heterofunctional αβ-Unsaturated Iminium Salts

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Data on the hydrolysis, aminolysis, hydrothiolysis, and cyanolysis of β-heterofunctional αβ-unsaturated aliphatic and cyclic iminium salts are described systematically and surveyed. The direction of attack by the nucleophile on the two C-electrophilic centres in these compounds is discussed.
The bibliography includes 81 references.

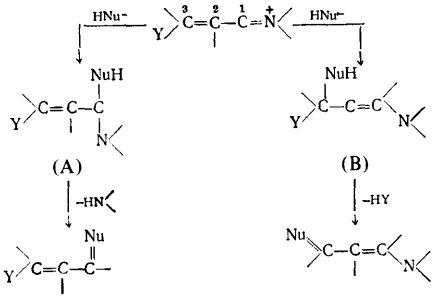
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I. INTRODUCTION

The many-faceted and high reactivity of compounds containing the $Y-\overset{|}{C}=\underset{|}{C}-\underset{|}{C}=\overset{+}{N}\diagdown$ (Y = HO, RO, SH, or Hal) group is of considerable theoretical and practical interest. However, there have been as yet no monographs or reviews devoted to the chemistry of such compounds. There exist only individual publications surveying the methods of synthesis and the properties of certain representatives of this class of substances [Freimanis[1] (p.183) and Liebscher and Hartmann[2]]. This review deals with the available few synthetic studies involving the nucleophilic substitution in β-heterofunctional αβ-unsaturated iminium salts, certain theoretical aspects of these reactions are discussed (in so far as this is allowed by the data obtained), and an attempt is made to assess their preparative importance.

The nucleophilic substitution reactions in activated unsaturated systems proceed in most cases via an "addition–elimination" mechanism.[3-5] Thus, when a charged nucleophile interacts with the $Y-\overset{|}{C}=\underset{|}{C}-\underset{|}{C}=\overset{+}{N}\diagdown X^-$ group, two intermediate adducts, (A) or (B), can be formed depending on the direction of attack [on the C(1) or C(3) atom].



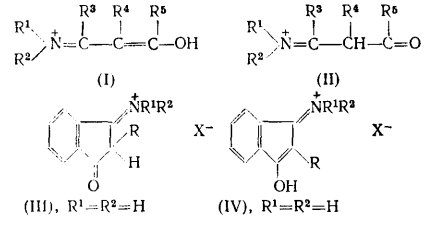
The outcome of the nucleophilic substitution in salts of the given type should apparently be subject to both charge and orbital control and the direction of the reaction should accordingly depend on the "hard–soft" properties of the nucleophile and both electrophilic centres in the substrate. Furthermore, in each specific case one must take into account the influence of the steric and electronic effects of the substituent in the pentad $Y-C(R^1)=C(R^2)-C(R^3)=\overset{+}{N}R^4R^5$, the acid–base properties of the medium, and the effects of solvation, temperature, and reaction time.

The first attempts to carry out calculations for the cations $Y-\overset{|}{C}=C-C=\overset{+}{N}\diagdown$ by the LCMO PPP method [Freimanis[1] (p.173) and Liebscher and Hartmann[2]] did not permit the elucidation of the specific reactivities of the C(1) and C(3) atoms. In only one investigation[6] was a more far-reaching quantum-mechanical analysis of nucleophilic substitution in 3-hetero-substituted cyclohex-2-ene-1-iminium salts carried out and a conclusion was reached about the preferred direction of the reactions of these salts with nucleophiles from the standpoint of the principle of "hard" and "soft" acids and bases (HSAB). The synthesis of certain new types of organic sulphur compounds became possible on the basis of these ideas.

II. β-HYDROXY AND β-ALKOXY-IMINIUM SALTS

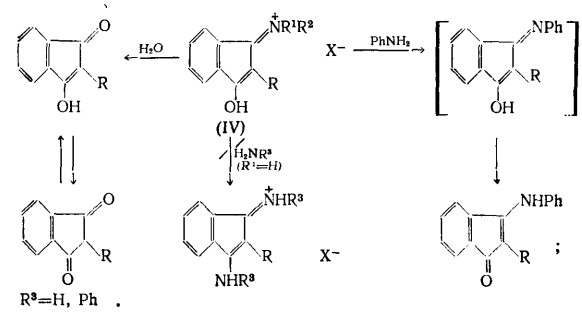
1. β-Hydroxyiminium salts

The reactivity of enaminoketones in nucleophilic substitution reactions is fairly low but increases appreciably in the presence of organic[7] or inorganic[8,9] acids. This can be explained by the intermediate formation in acidic media of the corresponding 3-hydroxyprop-2-eneiminium salts (I), which are highly electrophilic. Apart from protonation at the oxygen atom, there is a possibility of the C(2)-protonation with formation of the salt (II) [Freimanis[1] (p.187)]:



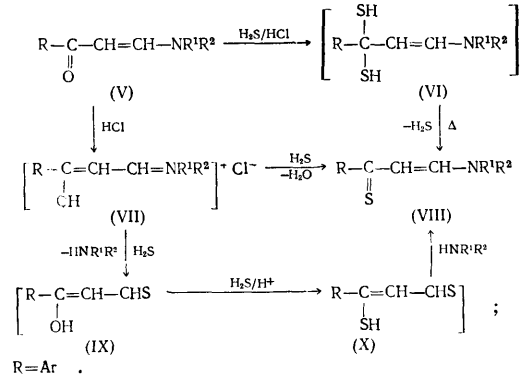
Precisely these two types of salts [compounds (III) and (IV)] were isolated among indene derivatives.[1] The form (III) is the most stable in the crystalline state. However, the reactions of enamines proceed as a rule in highly polar media, i.e. under conditions favourable for the existence of more polar tautomers—3-hydroxyind-2-eneiminium salts (IV).

Their behaviour has been investigated in hydrolysis and aminolysis reactions:[10]

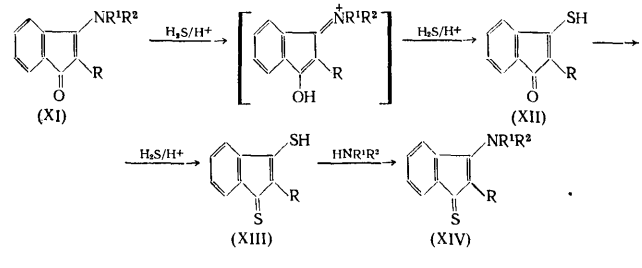


The preferred site of attack by the nucleophile in the salts (IV) is the $C=\overset{+}{N}$ bond. The explanation is that the solvated hydroxy-group is appreciably shielded and the nucleophilic species is directed towards the other electrophilic centre in the molecule.[10]

It has been suggested[1] that the hydrothiolysis of enaminoketones, which is usually carried out in alcoholic media in the presence of HCl, HF, or H_2SO_4, also proceeds via the intermediate hydroxypropeneiminium salt (VII). The second possible version of this reaction is believed to involve the intermediate formation of the *gem*-dithiol (VI).[11] Accordingly, the interaction of, for example, 1-aryl-3-(*NN*-dialkylamino)-1-propenones (V) with hydrogen sulphide in an alcoholic HCl solution[11–14] can be represented schematically as follows: (V) → (VI) → (VIII) and (V) → (VII) → (VIII).

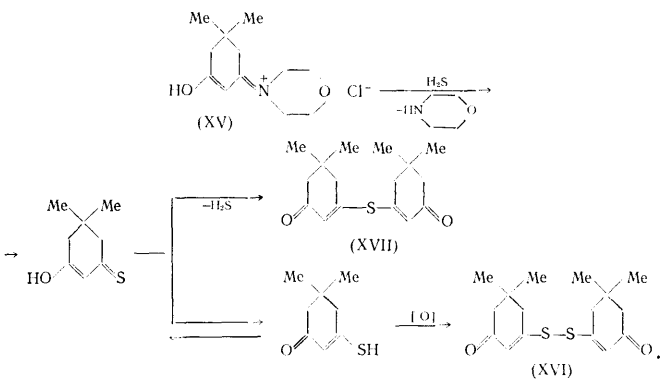


Bearing in mind the ability of various enaminoketones to form iminium salts with protic acids,[1,15,16] preference may be given to the intermediate (VII). However, the direct transformation (VII) → (VIII) is doubtful, since the reaction of 2-aryl-3-(*NN*-dialkylamino)-1-indenones (XI) with hydrogen sulphide in the presence of HCl in alcoholic media is accompanied by the thiolysis of the amino-group with formation of the mercaptoindenones (XII):[17]



Under the same conditions, compounds (XII) are converted into the β-dithiodiketones (XIII),[18] which readily react with highly basic amines to form the enaminothioketones (XIV).[19] For the same reason and also bearing in mind the mode of hydrothiolysis of the iminium salts,[6,20-23] one must postulate the more complex reaction scheme (V) → (VII) → (IX) → (X) → (VIII), which accounts for the low yield of the enaminothioketones (VIII) (3–10%).

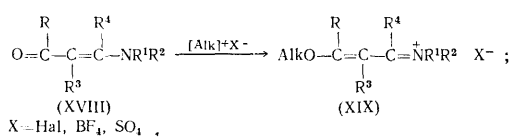
When 3-hydroxy-5,5-dimethylcyclohex-2-ene-1-*N*-morpholinium chloride (XV) reacts with hydrogen sulphide at −60 °C in dimethylformamide (DMF), the disulphide (XVI) and the sulphide (XVII) are present in the reaction mixture. Their formation indicates the attack by the nucleophile on the C=N̊ bond. The process probably proceeds in accordance with the mechanism[24]



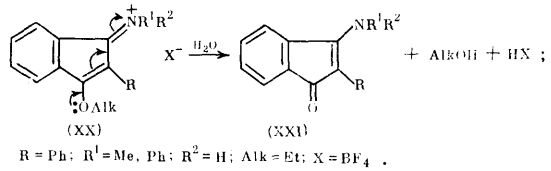
The benzeneiminium analogue of the salt (XV) does not react with hydrogen sulphide in the range from −60 °C to 15 °C, which indicates the low electrophilicity of this salt.

2. β-Alkoxyiminium Salts

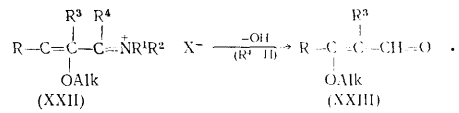
The salts (XIX) containing the β-alkoxypropeneiminium group are obtained by alkylating the corresponding enaminoketones (XVIII) by alkyl halides, dialkyl sulphates, or triethyloxonium tetrafluoroborate:[1]



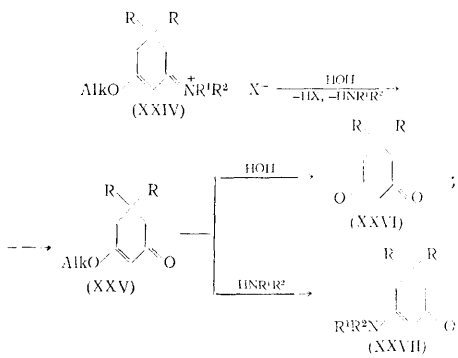
Hydrolysis. The salts containing the β-alkoxypropeneiminium group are much more sensitive to hydrolysis than the corresponding bases. Thus the tetrafluoroborates of 1-imino-3-ethoxyindenes (XX) are converted into the aminoindenones (XXI) even in the presence of traces of moisture.[25] The high lability of the salt (XX) can be explained by the increased electrophilicity of the C(3) atom in the cation induced by the strong electron-accepting effect of the iminium group. With increase of the latter, the stability of compounds (XX) falls. For example, the *N*-methyl-substituted salt (XX) initially dissolves in water and only then the enaminoketone (XXI) is formed. On the other hand, the *N*-phenyl-substituted compound (XX) is very hygroscopic and can be purified only in the form of the hydrolytically more stable free base:



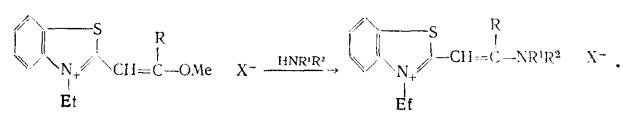
It was believed that salts of type (XX) are hydrolysed exclusively at the C(3)–O bond.[1] However, this is apparently true only for the hydrolysis of such compounds in neutral and acid media. Thus, when the salt (XXII) was treated with aqueous alkali, the aldehyde (XXIII), which is a product of the hydrolysis at the C(1) atom, was isolated:[26]



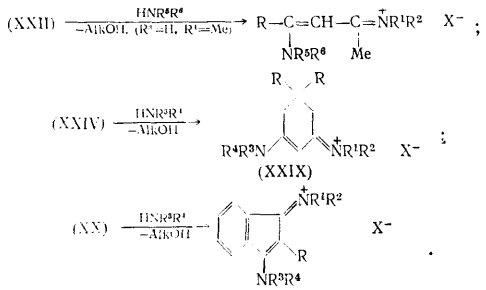
The hydrolysis of 3-alkoxycyclohex-2-ene-1-iminium salts (XXIV) in the presence of triethylamine at 20 °C also takes place at the C(1)=N̊ bond with elimination of amines and the formation of 3-alkoxycyclohex-2-en-1-ones (XXV).[27] After prolonged storage or heating of the reaction mixture, the product of further hydrolysis, namely the diketone (XXVI), and also the enaminoketone (XXVII) are formed. The latter is apparently obtained as a result of the reaction of the alkoxyketone (XXV) with the eliminated amine, which has been confirmed by the reaction of compound (XXV) with piperidine [the aminolysis of dimedone (XXVI) takes place under more severe conditions[28]]:



Aminolysis. The reactions of salts containing the β-alkoxypropeneiminium group with amines were first achieved for substituted benzothiazolium salts (XXVIII),[29] this being the only possible mode of reaction:



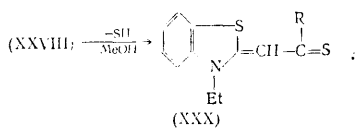
The aminolysis of other salts (aliphatic,[26,29] alicyclic,[23,28,30] and indene[31] salts) also takes place at the C(3)–O bond. These reactions are of great preparative importance for the synthesis of enaminoimines.[1] Other conditions being equal, the indene derivatives react more readily. This can be explained by the increased electrophilicity of the aryl substituent and hence by the greater reactivity of the C(3) atom. The reactions of aliphatic salts (XXII), the cyclohexene salts (XXIV), and the indene salts (XX) with 1,4-phenylenediamine in alcoholic media provide a clear example:[31]



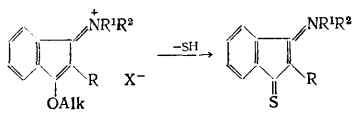
The rate of reaction depends on the basicity of the amine. Thus the reactions of *O*-alkyl derivatives of the cyclohexene enaminoketones (XXIV) with pyrrolidine in methanol take place instantaneously with evolution of heat and lead to the corresponding enaminoimine (XXIX) in a high yield (92%); the interaction of this salt with the less basic diethylamine is slow (48 h).[28]

In the aminolysis of salts with the 3-alkoxypropeneiminium group, the reaction involving the second electrophilic centre, namely the C(1) atom, was not observed. However, the overall data for the reactions of these compounds as well as their thio-analogues[32,33] with nucleophiles do not rule out the possibility of the amine exchange at the C(1) atom under certain conditions.

Hydrothiolysis and alkanethiolysis. When substituted benzothiazolium salts (XXVIII) react with alkali metal hydrogen sulphides, the alkoxy-group is readily substituted by the mercapto-group with formation of the enaminothioketones (XXX).[29] Subsequently this reaction became one of the preparative methods for the synthesis of enaminothioketones:



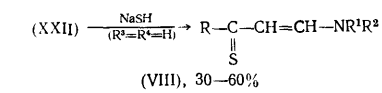
When 2-aryl-3-ethoxyindene-1-iminium tetrafluoroborates (XX) were heated with sodium hydrogen sulphide in methanol, a series of 3-amino-2-arylindene-1-thiones (XIV) were obtained.[34] The *N*-unsubstituted aminothioketones (XIVa–c) are formed in 55–74% yield. The yield of *N*-monoalkyl-substituted 3-amino-2-phenylindene-1-thiones (XIVe, f) is 31 to 38% and that of 2-phenyl-3-piperidinoindene-1-thione (XIVi) is below 30%. These data suggest that the reaction of the tetrafluoroborate (XX) and particularly that of the *NN*-disubstituted derivative (XXi) with sodium hydrogen sulphide can be determined to a large extent also by the attack of the *S*-nucleophile on the C=N bond with a subsequent wide range of different reactions:



(XX) (XIV)

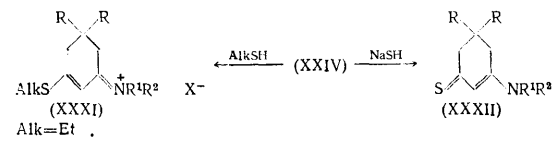
a) R=Ph, R^1=R^2=H; b) R=4-$MeOC_6H_4$, R^1=R^2=H; c) R=4-ClC_6H_4, R^1=R^2=H; d) R=1-$C_{10}H_7$, R^1=R^2=H; e) R=Ph, R^1=Me, R^2=H; f) R=Ph, R^1=$PhCH_2$, R^2=H; g) R=1-$C_{10}H_7$, R^1=Me, R^2=H; h) R=1-$C_{10}H_7$, R^1=$PhCH_2$, R^2=H; i) R=Ph, R^1R^2=$(CH_2)_5$;
Alk=Et; X=BF_4 .

The reactions of the salts (XXII) with sodium hydrogen sulphide are used to obtain aliphatic enaminothioketones (VIII):[35]



(VIII), 30–60%

N-Monosubstituted 3-ethoxy-5,5-dimethylcyclohex-2-ene-1-iminium salts (XXIV, R^1 = H; R^2 = Me or Ph; X = BF_4) react with sodium hydrogen sulphide in absolute alcohol at 20 °C to form a complex mixture of sulphur compounds, the corresponding enaminothioketones (XXXII) being obtained in a low yield (~9%):[36]



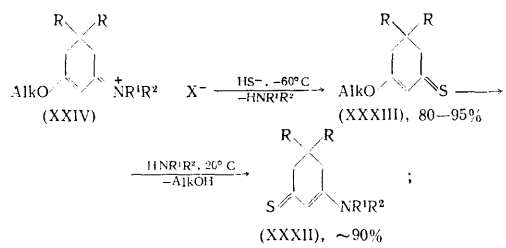
(XXXI) (XXXII)

Alk=Et .

Treatment of 3-ethoxy-5,5-dimethylcyclohex-2-ene-1-pyrrolidinium iodide [XXIV, R^1R^2 = $(CH_2)_4$; X = I] with ethanethiol in methanol in the presence of sodium methoxide at 25 °C led to a salt of the ethylthio-derivative (XXXI)† in 66% yield.[30]

In the instances of hydrothiolysis described above, the attack by the nucleophile on the C(3) atom in the propene fragment predominates. However, a recent systematic investigation of the hydrothiolysis of iminium salts with the cyclohexene skeleton led to a new idea about the mode of nucleophilic substitution in salts containing the 3-alkoxy-, 3-alkylthio-, and 3-chloropropeneiminium groups.[6,20–23] The results cast doubt on the apparently self-evident nature of the reaction of the HS^- anion at the C(3) atom in the compounds investigated.

Thus the study of the interaction of 3-alkoxycyclohex-2-ene-1-iminium salts (XXIV) with hydrogen sulphide or metal hydrogen sulphide at a low temperature established that the conversion of the initial compound (XXIV) into the enaminothioketones (XXXII) is a two-stage process:[23]



(XXIV) (XXXIII), 80–95% (XXXII), ~90%

R=H, Me; R^1=H, Alk, $-(CH_2)_n-$;
R^2=H, Alk, $-(CH_2)_n-$, Ar; X=BF_4, I .

The first stage, namely the hydrothiolysis of the C(1)=N bond and not the C(3)–O bond as was assumed previously, takes place at −60 to −40 °C and leads to previously unknown 3-alkoxycyclohex-2-ene-1-thiones (XXXIII) in a high yield. The second stage, namely the aminolysis of the stable intermediate (XXXIII), takes place at the C(3)–O bond and at 20 °C leads rapidly to a high yield of the enaminothioketones (XXXII).

The salts (XXIV) react with hydrogen sulphide only in a dipolar aprotic solvent [DMF, dimethyl sulphoxide (DMSO), hexamethylphosphoramide (HMP), and pyridine], known to

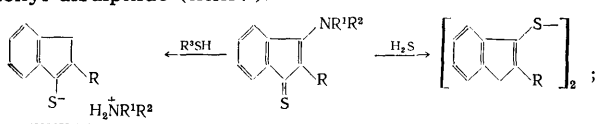
†One must bear in mind that the effective radius of the EtS^- anion is much greater than that of the HS^- anion[6] and that this may be responsible for the attack of the former on the sterically less hindered C–O bond.

be capable[37] of solvating the cations selectively and weakening the $H^+-{}^-SH$ bond, which increases the nucleophilicity of the hydrogen sulphide anion. Furthermore, the rate of nucleophilic substitution reactions is greatly influenced by the specific solvation of the anion.[38] The lower the degree of solvation of the anion, the higher its nucleophilicity and reactivity. Protic solvents solvate anions especially effectively owing to the tendency towards the formation of hydrogen bonds. In dipolar aprotic solvents the anions are less effectively solvated, i.e. here they behave as "true nucleophiles". In view of the necessary reaction temperature, a suitable solvent for the reaction (XXIV) → (XXXIII) is DMF.[6] The addition of a highly basic amine accelerates the process significantly and tends to increase the yield of the required product (XXXIII).

In a protic solvent (methanol, ethanol) the salts (XXIV) do not react with hydrogen sulphide at temperatures between −60° and 20 °C. When triethylamine or piperidine is added to the reaction mixture, only traces of compound (XXXIII) are formed. The salts (XXIV) react with sodium hydrogen sulphide in accordance with the scheme (XXIV) → (XXXIII) → (XXXII) both in DMF and in absolute methanol.[6,23]

At 20 °C, i.e. without the isolation of the intermediate (XXXIII), the reaction (XXIV) → (XXXII) terminates with a relatively low (~10%) yield of the enaminothioketone (XXXII). In this case the amine formed in the first stage is largely bound by the eliminated acid (HBF_4, $HClO_4$, HI) and hydrogen sulphide, which prevents the rapid occurrence of the subsequent reaction (XXXIII) → (XXXII).[6]

The reaction of 3-ethoxy-5,5-dimethylcyclohex-2-ene-1-*N*-piperidinium tetrafluoroborate [XXIV; R = Me; R^1R^2 = $(CH_2)_5$; Alk = Et; X = BF_4] with sodium hydrogen sulphide at 20 °C leads to the formation of a mixture of two thioketones (XXXII) and (XXXIII).[6,23] When the reaction is carried out in DMF at −60 °C with equimolar proportions of the initial compounds, the ethoxythioketone (XXXIII; Alk = Et) is formed preferentially, but, in the course of the treatment of the reaction mixture, it is almost fully converted into the enaminothioketone [XXXII; R^1R^2 = $(CH_2)_5$]. On the other hand, if acetic acid, which reduces the reactivity of piperidine, is added to the reaction mixture before this happens, it is possible to isolate the ethoxythione (XXXIII) in 54% yield. The yield of the enaminothioketone (XXXII) also depends on the competing reactions of compounds (XXXII) and (XXXIII) with *S*-nucleophiles. For example, the indene analogues (XIV) of compounds (XXXII) are readily reduced by thiols or hydrogen sulphide, forming the thiolates (XXXIV) [39] or bisindenyl disulphide (XXXV):[34]

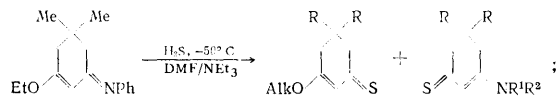


(XXXIV) (XIV) (XXXV)

R=Ph; R^3=Bu, Ph, H .

The multistage reaction (XXIV) → (XXXIII) → (XXXII) is followed by TLC and spectrometrically. For example, it has been found that, for R = OMe, R^1R^2 = $(CH_2)_2O(CH_2)_2$, R^3 = Me, and X = I, the above process is accompanied by the consecutive bathochromic and then hypsochromic shifts of the long-wavelength absorption band in the electronic spectrum—the colourless solution becomes raspberry-red and then yellow: λ_{max} = 286 nm ($\lg\varepsilon$ = 3.8) → λ_{max} = 498 nm ($\lg\varepsilon$ = 4.6) → λ_{max} = 386 nm ($\lg\varepsilon$ = 4.4).[6]

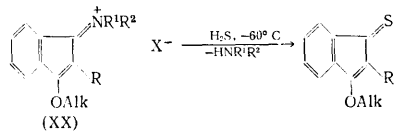
It must be emphasised that the hydrothiolysis of only the *NN*-disubstituted iminium salts (XXIV) at a low temperature leads exclusively to compounds (XXXIII).[6] The *N*-monosubstituted salts (XXIV) react with hydrogen sulphide in DMF in the presence of triethylamine to form a mixture of products containing small amounts of the alkoxythioketone (XXXIII) and the corresponding enaminothioketone (XXXII). This can be explained by the fact that in basic media the *N*-monosubstituted salts (XXIV) are deprotonated and are readily converted into the less reactive bases with the RO−C=C−C=N− group. Their hydrothiolysis can take place at the C(1) and (or) C(3) atoms[1] and should require more severe conditions. Thus a long time is required for the completion of the reaction of 3-ethoxy-5,5-dimethyl-1-phenylcyclohex-2-ene (XXXVI) with hydrogen sulphide; ultimately a mixture of products containing the ethoxythioketone (XXXIII) and the N-phenyleneaminothioketone (XXXII) is formed:[23]



(XXXVI) (XXXIII) (XXXII)

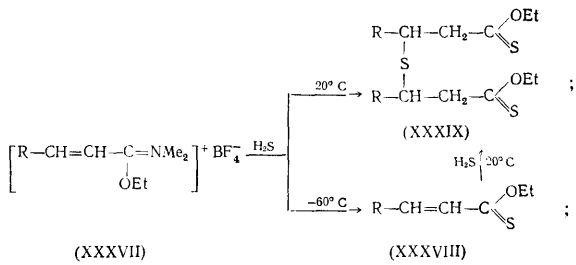
R=Me, R^1=H, R^2=Ph, Alk=Et .

The results of the hydrothiolysis of the cyclohexeneiminium salts (XXIV) have been confirmed in relation to the indene compond (XX):[40]



(XX)

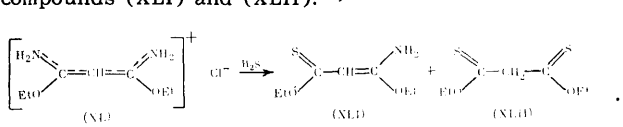
The hydrothiolysis of 1-alkoxyprop-2-eneiminium salts (XXXVII), the structural isomers of substituted cyclohexenes (XXIV), which takes place at −15 °C in a mixture of anhydrous ether and pyridine, is remarkable from this point of view. This reaction proceeds with elimination of the amine and retention of the C−O bond. Whereas at −60 °C the hydrothiolysis of the salt (XXXVII; R = Me) leads to compound (XXXVIII), the sulphide (XXXIX) was isolated at 20 °C. The latter is formed as a result of the addition of hydrogen sulphide to the C=C bond and subsequent intermolecular condensation:[41,42]



(XXXVII) (XXXVIII)

R=Me, Ph .

The reactions of the salts (XL) with hydrogen sulphide in a methanol–pyridine mixture proceed analogously with formation of compounds (XLI) and (XLII):[41,43]



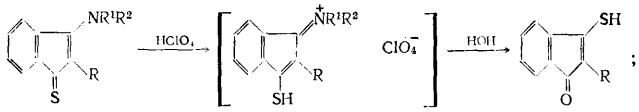
(XL) (XLI) (XLII)

III. β-MERCAPTO- AND β-ALKYLTHIO-IMINIUM SALTS

1. β-Mercaptoiminium Salts

Stable 3-mercaptoprop-2-eneiminium salts and their cyclic analogues are known. It has been shown by ^{1}H NMR [44] that 3-(*NN*-dimethylamino)-2-phenyl-1-indenethione (XIV) is

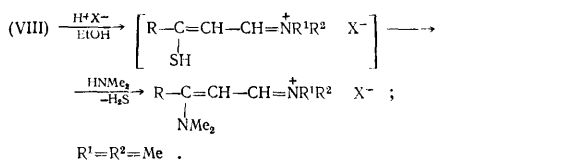
protonated by perchloric acid in acetone with formation of a solution of 3-mercapto-*NN*-dimethyl-2-phenylindene-1-iminium perchlorate (XLIII). The latter hydrolyses at the C=N bond and is converted into 3-mercapto-2-phenyl-1-indenone (XII):



(XIV) (XLIII) (XII), 80%

R=Ph; R^1=R^2=Me .

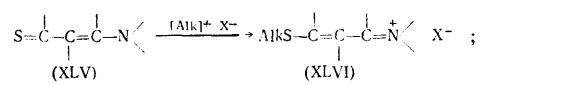
A mechanism has been proposed for the aminolysis of 3-aminoprop-2-enethione (VIII) in an acid medium at 20 °C, in which the intermediate formation of the 3-mercaptoprop-2-eneiminium salt (XLIV) is postulated:[11]



R^1=R^2=Me .

2. β-Alkylthioiminium Salts

The salts (XLVI), containing the β-alkylthiopropeneiminium group, are obtained from the corresponding enaminothioketone (XLV) using the same alkylating agents as in the synthesis of their 3-alkoxy-analogues (see above). Methyl fluorosulphonate is used for this purpose:[45]

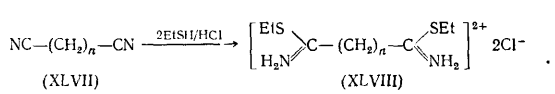


(XLV) (XLVI)

X=Hal, BF_4, FSO_3, SO_4 .

Stable salts of the propene,[46,47] indene[48] and cyclohexene[6] series and the thio- and dithio-esters of squaric[49] and dicarboxylic[43] acids have been synthesised in this way in high yields. Enaminothioketones are alkylated regiospecifically and more readily than enaminoketones.[21,48]

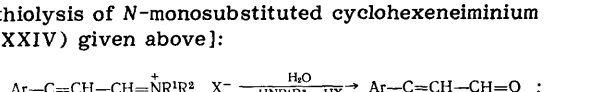
Dicarboxylic acid thioesters (XLVIII) are also obtained by the reaction of the corresponding dinitriles (LXVII) with ethanethiol and hydrogen chloride:[43,50]



(XLVII) (XLVIII)

Hydrolysis. The few studies which have been made on the hydrolysis of β-alkylthio-substituted αβ-unsaturated iminium salts nevertheless embrace compounds of various classes, which makes it possible to discover a general feature of the process—the direction of attack by the hydroxide ion on the C=N bond.

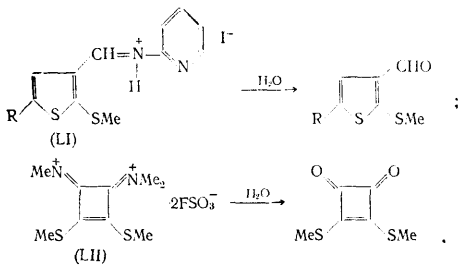
The hydrolysis of *NN*-disubstituted 3-methylthioprop-2-eneiminium salts (XLIX) leads to the corresponding β-alkylthioaldehydes (L).[46,47,51] The *N*-monoaryl-substituted iodides (XLIXb) are hydrolytically stable [cf. data on the hydrothiolysis of *N*-monosubstituted cyclohexeneiminium salts (XXIV) given above]:



(XLIX) (L)

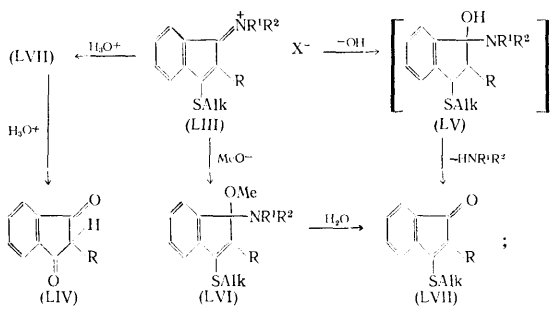
Ar=Ph, 4-ClC_6H_4, 4-$MeOC_6H_4$; R^1R^2=$(CH_2)_4$, $(CH_2)_5$, $(CH_2)_2O(CH_2)_2$ (a); R^1=H, R^3=Ar (b); X=I .

The salts of the thiophen series (LI)[52] as well as derivatives of squaric acid (LII) are hydrolysed analogously:[45]



(LI) (LII)

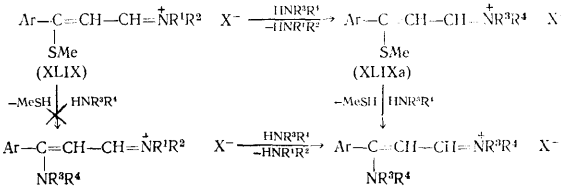
The hydrolysis of 3-alkylthio-2-phenylindene-1-*NN*-dimethyliminium salts (LIII) has been studied in greatest detail.[48] Alkaline hydrolysis in DMF leads to their ready conversion into 3-alkylthio-2-phenyl-1-indenones (LVII). The *gem*-alcohols (LV) are probably intermediates in this reaction, since the corresponding *gem*-methoxyamino-derivatives were isolated on methanolysis of the salt (LIII). Their hydrolysis leads to the alkylthioketones (LVII). The final product of the acid hydrolysis of the salt (LIII), which proceeds via the formation of the alkylthioketones (LVII), is 2-phenyl-1,3-indandione (LIV):[48]



(LIV) (LVI) (LVII)

R = Ph; R^1=R^2=Me .

Aminolysis. 3-Alkylthiopropeneiminium salts (XLIX) react with alkyl- and aryl-amines to form the salts of enaminoimines with identical substituents at different nitrogen atoms [compounds (LVIIIa)].[32,33] Of the two possible reactions (XLIX) → (LVIII) → (LVIIIa) and (XLIX) → (XLIXa) → (LVIIIa), the latter occurs.[32] The sequence of reaction stages (transamination–substitution) has been demonstrated by the reaction of compound (LVIIIa; Ar = 4-$MeOC_6H_4$; R^3 = R^4 = Et; X = ClO_4) with an excess of dimethylamine. It was found that the reaction of the resulting asymmetrically substituted salt [4-$MeOC_6H_4$–C(NMe_2)=CH–CH=NEt_2]$^+ClO_4^-$ dimethylamine, modelling the stage (LVIII) → (LVIIIa), does not take place:



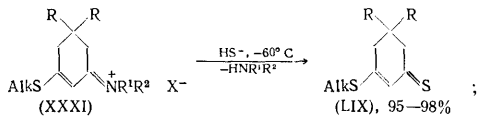
(XLIX) (XLIXa) (LVIII) (LVIIIa)

Ar=Ph, 4-$MeOC_6H_4$; R^1=R^2=Alk; R^3=R^4=Alk или R^3 = H, R^4=Ar; X = ClO_4, I .

When the salts (XLIX) are acted upon by arylamines in ethanol, the transamination products (XLIXa) are formed in 90% yield. The methylthio-group is exchanged for the amino-group [(XLIXa) → (LVIIIa)] only in acetic acid.[33] The perchlorates (XLIX; Ar = Ph or 4-$MeOC_6H_4$; X = ClO_4) form

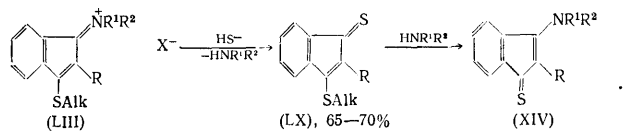
the corresponding enaminoimines (LVIIIa) in a high yield (up to 88%). On the other hand, the enaminoimine salts (LVIIIa) are obtained from the analogous iodides (XLIX) in a yield not exceeding 38%.

Hydrothiolysis. The study of the reactions of β-alkylthio-substituted αβ-unsaturated iminium salts with sulphur-containing nucleophiles was first undertaken in relation to cyclohexene derivatives.[6,21] 3-Alkylthiocyclohex-2-ene-1-iminium salts (XXXI) react with hydrogen sulphide in DMF in the presence of triethylamine at −60 °C via the C=N bond (see above), similarly to the 3-alkoxy-derivatives, forming 3-alkylthiocyclohex-2-ene-1-thiones (LIX). These compounds contain the little known structural fragment AlkS−C=C−C=S:

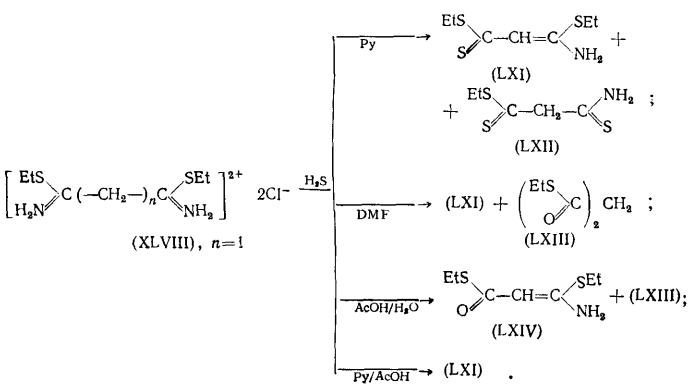


R^1=H, Alk, $-(CH_2)_n-$; R^2=H, Alk, $-(CH_2)_n-$, Ar; X=BF_4, I .

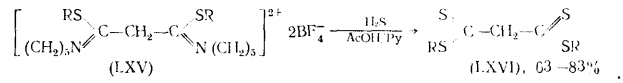
3-Alkylthio-2-arylindene-1-iminium salts (LIII) react with hydrogen sulphide in methanol at 20 °C to form 3-alkylthio-2-arylindene-1-thiones (LX). When the salt (LIII) is treated with sodium hydrogen sulphide, the corresponding enaminothioketones (XIV) are formed rapidly in accordance with the scheme (LIII) → (LX) → (XIV):[48]



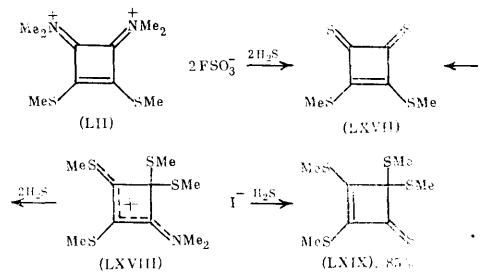
The hydrothiolysis of the dihydrochloride of *SS*-diethylpropanedithiodiimidic acid (XLVIII) has been investigated in detail.[50] This salt does not interact with liquid hydrogen sulphide at −78 °C, while at 20 °C in pyridine, DMF, DMSO, or acetic acid, several compounds (LXI)–(LXIV) are formed in yields ranging from 20 to 40%, which indicates the non-regiospecificity of the hydrothiolysis. The formation of the carbonyl compounds (LXIII) and (LXIV) has been explained[50] by the hydrolysis of the initial dihydrochloride (XLVIII) as a result of the treatment of the reaction mixture with an aqueous solution of sodium bicarbonate:



N-Unsubstituted salts (XLVIII) react with hydrogen sulphide in a pyridine–acetic acid mixture, retaining one amino-group, while their piperidine analogues (LXV) lose both amino-groups under these conditions and give rise to the ester of the bisdithiocarboxylic acid (LXVI):[41]

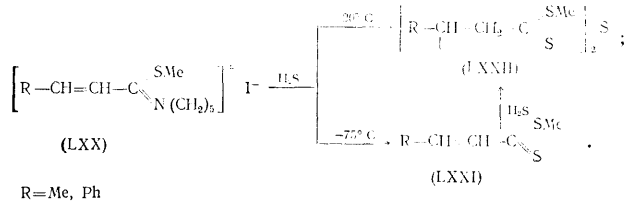


The hydrothiolysis of both dimethylamino-groups in methylthiocyclobut-2-ene-1,4-bis-*NN*-dimethyliminium bisfluorosulphonate (LII) proceeds readily. The product of this reaction is 2,3-bis(methylthio)cyclobut-2-ene-1,4-dithione (LXVII), whose chemical properties have been vigorously investigated:[49,53]



The hydrothiolysis of 2,3,4,4-tetrakis(methylthio)cyclobut-2-ene-1-*NN*-dimethyliminium iodide (LXVIII) either proceeds immediately via two pathways to the dithiodiketone (LXVII) or the reaction involves only the iminium group, which leads to the monothioketone (LXIX).[53]

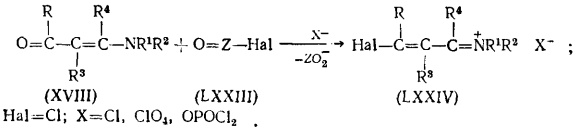
1-Methylthioprop-2-ene-1-piperidinium iodide (LXX), which is a structural isomer of the 3-alkylthioprop-2-ene-1-iminium salts (XLIX), reacts with hydrogen sulphide in a tetrahydrofuran (THF)—pyridine mixture at −75 °C, forming methyl dithiocinnamate (LXXI).[42] The sulphide (LXXII) has been obtained at 20 °C by the reaction of compound (LXX) with hydrogen sulphide (cf.the reaction described in Section III, 2 above):



R=Me, Ph

IV. β-HALOGENOIMINIUM SALTS

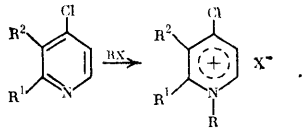
There exist two main synthetic approaches to the preparation of β-halogeno-substituted αβ-unsaturated iminium salts (LXXIV).[2] The first is based on the corresponding modification of the C(1)- and C(3)-structural elements in the initial compound with the propene group. The second involves the construction of the propene skeleton of the salt from suitable components containing the C(1)- and C(2)-, C(3)-fragments of the required compound. Halogenoiminium salts are obtained by the first method as a result of the interaction of β-aminovinylcarbonyl compounds (LXXX) with various chlorinating agents (LXXIII) ($POCl_3$, $COCl_2$, SO_2Cl_2, and ClCOCOCl) or even with PCl_5. Treatment with the analogous brominating agents leads to the corresponding bromo-substituted salts. Compounds (XVIII) and (LXXIII) vary structurally within relatively wide limits:[28]



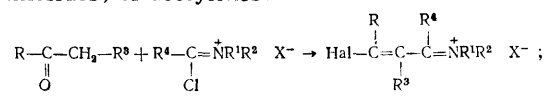
(XVIII) (LXXIII) (LXXIV)

Hal=Cl; X=Cl, ClO_4, $OPOCl_2$.

The first method is also used to synthesise substituted pyridinium salts by alkylating 4-chloropyridines:[2]



In the synthesis of 3-chloroprop-2-eneiminium salts (LXXIV) via the formation of the C(1)–C(2) bond, one uses methyleneketones and the salts of imidoyl chlorides, mainly formimidoyl chloride, or even the phosgeneiminium salt, whose mobile chlorine atom is readily substituted by a nucleophile.[2] The initial methylenecarbonyl compound can be replaced, for example, by enamines, enol ethers, acetals, vinyl chlorides, or acetylenes:[2]

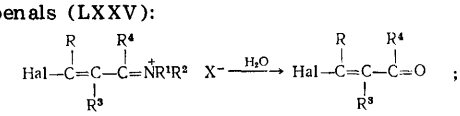


(LXXIV)

R^4=H, Cl; Hal=Cl .

The second method is of the greatest synthetic importance. However, the first method is so far the only one available in many instances, for example, for cyclic derivatives.

Hydrolysis. Little information is available about the hydrolysis of 3-halogenoprop-2-eneiminium salts and their cyclic analogues.[54–56] 3-Halogeno-prop-2-ene-1-*NN*-dimethyliminium salts (LXXIV) are hydrolysed with retention of the C–Hal bond, which leads to the formation of 3-halogenopropenals (LXXV):

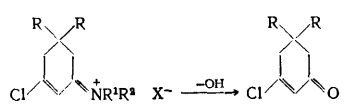


(LXXIV) (LXXV)

R^4=H; Hal=Br, Cl; X=Cl, ClO_4, $OPOCl_2$, *o*-$MeC_6H_4SO_2O$.

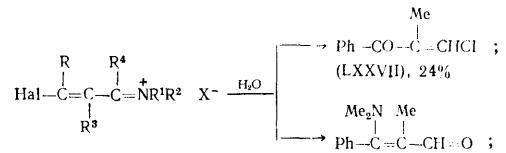
The nature of the substituents R and R^3 has a marked effect on the hydrolytic stability of the salts (LXXIV). The salts (LXXIV; R^1 = H or Me; R^3 = H), which have no substituents at the central carbon atom, are distinguished by an extremely high stability in aqueous solution, which can be accounted for[56] by the high degree of conjugation in the pentad fragment.

The salts (LXXIV) having substituents R with a large effective volume (R = Ph or t-Bu) and R^3 = H are readily hydrolysed on refluxing with an aqueous solution of sodium acetate. 3-Chlorocyclohex-2-ene-1-pyrrolidinium perchlorate (LXXVI) is also hydrolysed at the C=N̊ bond on heating in methanol to which a 10% NaOH solution has been added:[28]



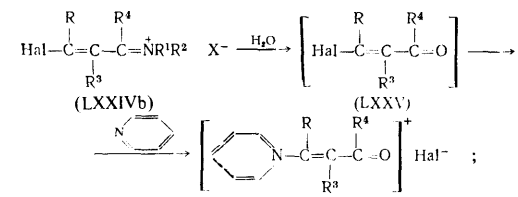
(LXXVI) 95%

3-Chloro-2-methyl-1-phenylprop-2-ene-1-*NN*-dimethyliminium chloride (LXXIVa) is hydrolysed via two pathways with formation of 3-chloro-2-methyl-1-phenylprop-2-en-1-one (LXXVII) and more than 50% of the aldehyde (LXXVIII). The low yield of the ketone (LXXVII) can be accounted for by steric hindrance, which prevents the hydrolysis of the C=N̊ bond:[54]



(LXXIV a), R=H, R^1=R^2=R^3=Me, R^4=Ph, Hal=X=Cl .

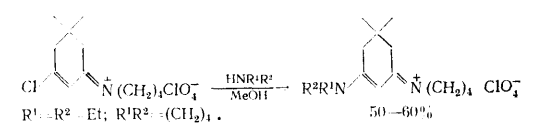
Treatment of the 3-chloro-3-(4-tolyl)prop-2-ene-1-iminium salt (LXXIVb) with pyridine in 90% ethanol yielded the chloride (LXXIX).[57] It may be that the first stage of this reaction is the hydrolysis of the salt (LXXIVb) at the C=N̊ bond and the formation of 3-chloropropenal (LXXV), whose aminolysis at the C–Cl bond leads to compound (LXXIX):



(LXXIVb) (LXXV) (LXXIX)

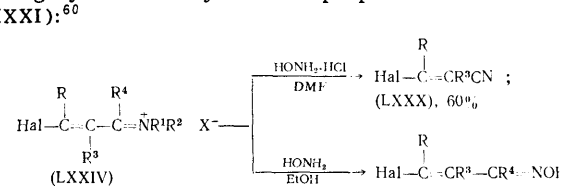
R=4-MeC_6H_4, R^3=R^4=H, Hal=Cl .

Aminolysis. β-Chloro-substituted αβ-unsaturated iminium salts react with amines, substituting the chlorine atom for the amino-group, which leads to salts of enaminoimines,[28,58] for example:



R^1=R^2=Et; R^1R^2=$(CH_2)_4$. 50–60%

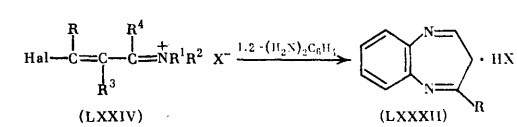
The ability of chloroiminium salts to react with nucleophiles via the C=N̊ bond has attracted much attention by investigators. Thus the reaction of arylpropene derivatives (LXXIV) with hydroxylamine hydrochloride in DMF has led to a simple way of synthesising the corresponding 3-chloropropenyl cyanides (LXXX).[59] Treatment of the salt (LXXIV) in ethanol with a hot aqueous solution of hydroxylamine leads to a high yield of 3-aryl-3-chloroprop-2-ene-1-aldoxime (LXXXI):[60]



(LXXIV) (LXXX), 60% (LXXXI), 92%

R=4-MeC_6H_4, 4-$MeOC_6H_4$; R^3=R^4=H; Hal=Cl .

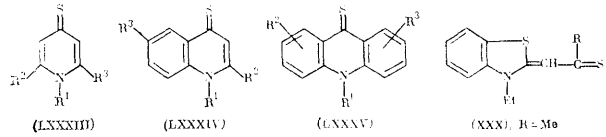
When the salts (LXXIV) react with 1,2-phenylenediamine, both electrophilic centres—the C(1) and C(3) atoms—are attacked by the nucleophile and 2-aryl-3*H*-1,5-benzodiazepinium salts (LXXXII) are formed:[61]



(LXXIV) (LXXXII)

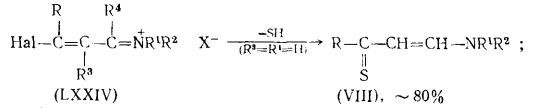
R=Ar, R^3=R^4=H, Hal=Cl .

Hydrothiolysis. The reactions of salts of nitrogen-containing heterocyclic bases incorporating the $Cl-\overset{|}{C}=C-\overset{|}{C}=\overset{+}{N}\diagdown X^-$ group with sodium sulphide of hydrogen sulphide in alcohol has been used for a long time to synthesise the corresponding heterocyclic enaminothioketones. Sodium thiosulphate and *NN*-dimethyldithiocarbamate,[62] and thiourea[63] have also been used for the thiolysis of salts of this type. Substituted 4-thiopyridones (LXXXIII),[63,64] 4-thioquinolones (LXXXIV),[64,65] 9-thioacridones (LXXXV),[62,66,67] and 3-ethyl-2-thioacetonylidene-2,3-dihydro-1,3-benzothiazole (XXX)[68] have been obtained in this way in high yields:



(LXXXIII) (LXXXIV) (LXXXV) (XXX), R=Me

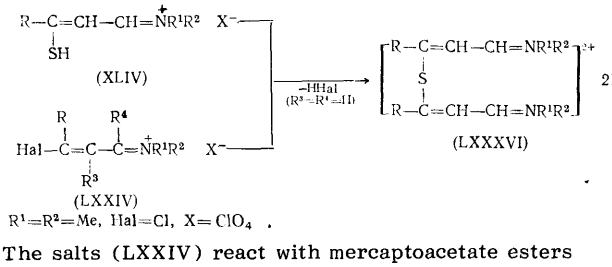
The synthesis of the aliphatic enaminothioketones (VIII) is based on the reactions of 3-aryl-3-chloroprop-2-ene-1-*NN*-dimethyliminium salts (LXXIV) with sodium sulphide in aqueous DMF solution or in a DMF–ethylene glycol mixture[69] and also with sodium thiosulphate in alcohols.[70] The temperature (20–60 °C) and the reaction time (2–24 h) are determined by the nature of the aryl substituent:



(LXXIV) (VIII), ~80%

R=Ph, 4-MeC_6H_4, 4-BrC_6H_4, 1-$C_{10}H_7$ etc.; $R^1=R^2=Me$; Hal=Cl .

When the reaction mixture is treated with a primary or secondary amine, amine exchange takes place and leads to the corresponding enaminothioketones $R-C(=S)-CH=CH-NR^1R^2$ (VIII) with a wide variety of nitrogen-containing substituents.[70] If the molar ratio of sodium thiosulphate and the salt (LXXIV) is 1:2, the reaction product is the sulphide compound (LXXXVI) (yield 80%). It is apparently obtained as the final result of the condensation of the initial 3-chloropropeneiminium salt (LXXIV) with the 3-mercaptopropeneiminium salt (XLIV) formed initially:

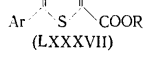


(XLIV) (LXXXVI)

(LXXIV)

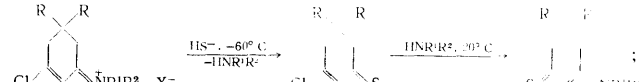
$R^1=R^2=Me$, Hal=Cl, X=ClO_4 .

The salts (LXXIV) react with mercaptoacetate esters $HSCH_2COOR$ in the presence of sodium methoxide with elimination of the chlorine atom and the amino-group and the formation of cyclisation products—5-substituted thiophencarboxylates (LXXXVII):[71]



(LXXXVII)

Thus, until recently, the usual pathway in the reaction of compounds containing the $Cl-\overset{|}{C}=C-\overset{|}{C}=\overset{+}{N}\diagdown$ group with sulphur-containing nucleophiles was believed to involve the substitution of the chlorine atom. However, it was established in 1979[2] that this reaction can proceed with dissociation of the C=N bond. Thus the interaction of 3-chlorocyclohex-2-ene-1-iminium salts (LXXVI) with hydrogen sulphide in DMF at −60 °C in the presence of triethylamine leads to 3-chlorocyclohex-2-ene-1-thione (LXXXVIII). A compound containing the $Cl-\overset{|}{C}=C-\overset{|}{C}=S$ group was obtained in this way for the first time. The chlorothione (LXXXVIII) is a stable intermediate in the hydrothiolysis of the salt (LXXVI), since it interacts instantaneously with amines at 20 °C, forming the enaminothioketones (XXXII):[6,22]

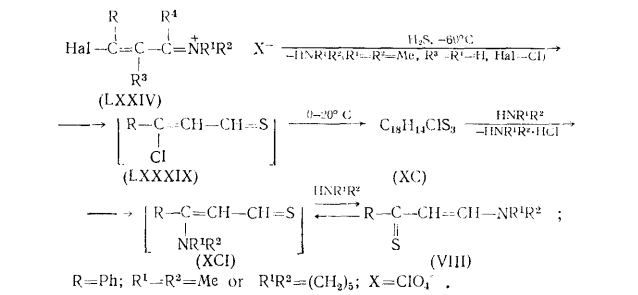


(LXXVI) (LXXXVIII), 87% (XXXII)

R^1=H, Alk, $-(CH_2)_n$; R^2=H, Alk, $-(CH_2)_n$, Ar; X=ClO_4 .

In addition it has been established[6] that the reaction of 3-chloro-3-phenylprop-2-ene-1-*NN*-dimethyliminium perchlorate (LXXIV) with hydrogen sulphide in DMF at −60 °C entails in the first place the elimination of dimethylamine, and not hydrogen chloride, and compound (XC) having the composition $C_{18}H_{14}ClS_3$ is produced. In this case the hydrothiolysis of the iminium group should have led to 3-chloro-3-phenylprop-2-ene-1-thial (LXXXIX), but the latter could not be isolated in a pure state. The absence of resolved signals in the IR, ^{13}C NMR, and ^1H NMR spectra of the product (XC) indicated its polymeric structure.

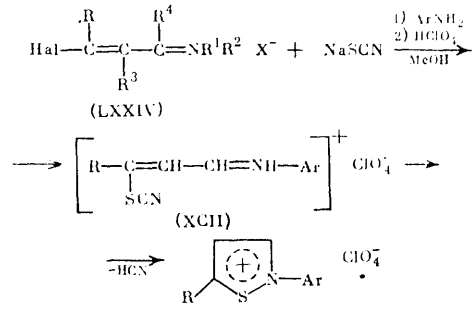
The hydrothiolysis product (XC) reacts rapidly with dimethylamine and piperidine at 20 °C.[6] The amine hydrochlorides isolated under these conditions indicate the involvement of the C–Cl bond in the reaction. However, the aminolysis products were not 3-(*NN*-dimethylamino)-(piperidino)-3-phenylprop-2-ene-1-thials (XCI) or the isomeric enaminothioketones (VIII), identical with those described previously.[70] Like their oxygen analogues,[55,72] the thials (XCI) formed initially probably isomerise in the presence of amines, which is the reason for the final outcome of the aminolysis of the product (XC):



(LXXIV) (LXXXIX) (XC) (XCI) (VIII)

R=Ph; $R^1=R^2=Me$ or $R^1R^2=(CH_2)_5$; X=ClO_4 .

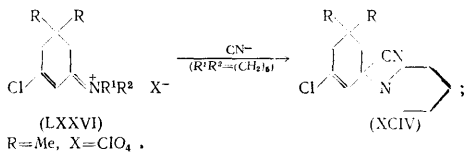
Reaction with alkali metal thiocyanates. The successive interaction of 3-chloroprop-2-ene-1-iminium salts (LXXIV) with thiocyanic acid and primary aromatic amines leads to 1,2-thiazolium salts (XCIII).[2] The authors[2] suggest that the reaction proceeds via the intermediate formation of 3-thiocyanatoprop-2-ene-1-iminium salts (XCII):



(LXXIV) (XCII) (XCIII), 27%

The reactions of the salts $ClCR{=}CH{-}CH{=}\overset{+}{N}R^1R^2\ X^-$ with KSCN (or NaSCN) in acetonitrile or DMF in the presence of catalytic amounts of tetra-alkylammonium iodide or crown-ether lead to 3-thiocyanato-substituted salts $NCSCR{=}CH{-}CH{=}\overset{+}{N}R^1R^2\ X^-$, where R = Ph, Ar, naphthyl, anthryl, heteroaryl, or PhCH = CH, R^1, R^2 = Alk, Ar or $R^1R^2 = (CH_2)_4$ or $(CH_2)_2O(CH_2)_2$, and X = Cl, ClO_4, or PO_2Cl_2, in 44–97% yield.[73]

Cyanolysis. The product of the reaction of 3-chloro-5,5-dimethylcyclohex-2-ene-1-piperidinium (LXXVI) with potassium cyanide in DMF is 3-chloro-1-cyano-5,5-dimethyl-1-piperidinocyclohex-2-ene (XCIV):[6]

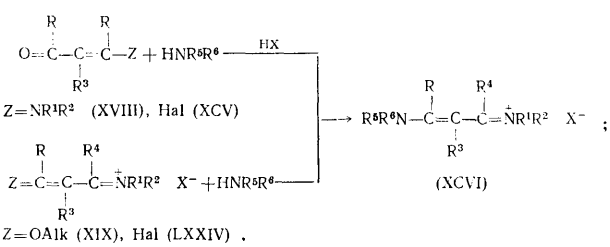


(LXXVI)
R=Me, X=ClO_4 .

The formation of the geminal aminonitrile (XCIV) shows that, in the first stage of the overall nucleophilic substitution reaction involving salts of type (LXXVI), the "soft" nucleophile adds to the $C(1){=}\overset{+}{N}$ bond and not to the C(2)=C(3) bond.

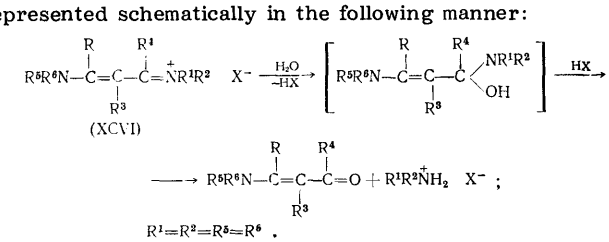
V. β-AMINOIMINIUM SALTS

The reactions of compounds (XVIII) containing the β-aminovinylketone group or compound (XCV) containing the β-halogenovinylketone groups as well as the reactions of β-heterofunctional αβ-unsaturated iminium salts (XIX) and (LXXIV) with various amines are usually employed for the synthesis of enaminoimine salts (XCVI):[1]



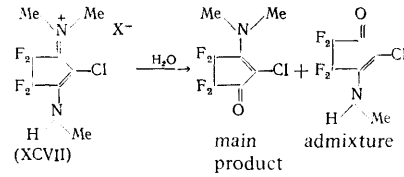
Z=OAlk (XIX), Hal (LXXIV) .

Hydrolysis. The hydrolysis of the enaminoimine salts (XCVI) substituted symmetrically at the nitrogen atoms can be represented schematically in the following manner:



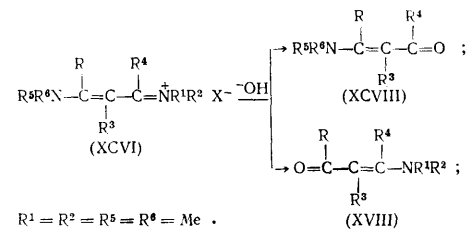
Depending on the structure of the salts, this reaction takes place in acid, neutral, or basic media.[1] The *N*-aryl-substituted salts of the indene enaminoimines are more resistant to hydrolysis than those unsubstituted at the nitrogen atom.[74]

In the case of asymmetrically substituted enaminoimine salts, the question arises of the carbon atoms to which the attack by the nucleophile is directed. The influence of steric factors on the outcome of the hydrolysis has been stressed in a study[75] of the hydrolysis of the 2-chloro-4,4,5,5-tetrafluoro-3-(*N*-methylamino)cyclopent-2-ene-1-*NN*-dimethyliminium salt (XCVII) and also in a review:[1]



(XCVII) main product admixture

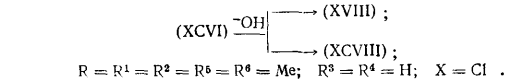
The mode of hydrolysis of tetrasubstituted aminopropeneimine salts (XCVI) is treated from the same standpoints:[1]



$R^1 = R^2 = R^5 = R^6 = Me$.

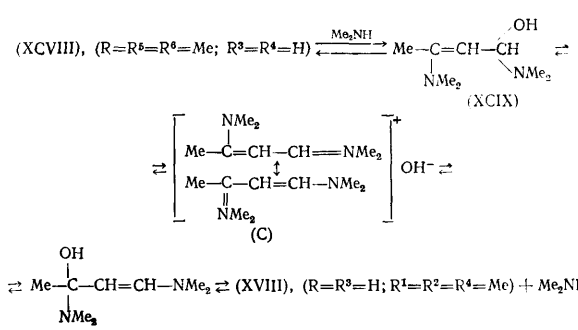
When R = Me or Ph and R^4 = H, mainly the enaminoaldehyde (XCVIII) is formed, while the isomer (XVIII) is a side product.

In another study[76] the mechanism of the reactions was treated in a different way. Two isomers, namely 4-(*NN*-dimethylamino)but-3-en-2-one (XVIII) and 3-(*NN*-dimethylamino)but-2-en-1-al (XCVIII), were isolated on hydrolysis of 3-methyl-3-(*NN*-dimethylamino)prop-2-ene-1-*NN*-dimethyliminium chloride (XCVI) with aqueous alkali:



R = $R^1 = R^2 = R^5 = R^6$ = Me; $R^3 = R^4$ = H; X = Cl .

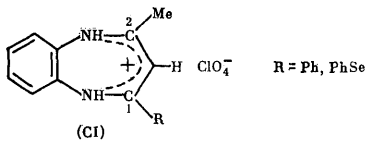
The hydrolysis of the salt (XCVI) at 25 °C and a reduced pressure leads to the aldehyde (XCVIII) in 55% yield. The authors[76] explained the formation of the two isomers (XVIII) and (XCVIII) on hydrolysis of the salt (XCVI) by the ability of the aldehyde (XCVIII) to isomerise readily to the ketone (XVIII) on treatment with dimethylamine. It was suggested that the *gem*-hydroxyamine (XCIX), formed as a result of the addition of dimethylamine to the aldehyde (XCVIII), is in equilibrium with the dissociated form (C). Its mesomeric cation is converted into the aldehyde (XCVIII) or the ketone (XVIII) after recombination with a hydroxide ion and the elimination of dimethylamine:



(C)

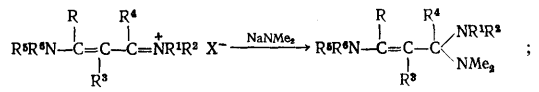
The mode of hydrolysis of enaminoimine salts is also influenced by the electronic nature of the substituents. Thus, in the hydrolysis of benzodiazepinium salts (CI),[76,77] the electronic effects of the substituents are decisive, because

the hydroxide ion attacks the sterically most shielded C(1) atom:



(CI) R = Ph, PhSe

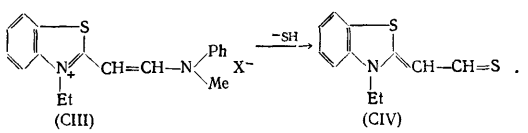
Aminolysis. The aminolysis of enaminoimine salts is usually terminated by transamination and has little preparative value.[78] The reaction probably proceeds via the formation of a *gem*-diamine. When 3-(*NN*-dimethylamino)prop-2-ene-1-*NN*-dimethyliminium salts (XCVI) were allowed to react with sodium NN-dimethylamide in benzene, the stable aminal (CII) was obtained:[79]



(XCVI) (CII), 62%

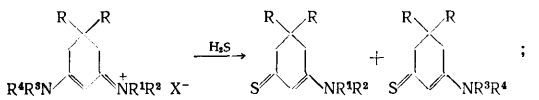
$R = R^3 = R^4 = H$; $R^1 = R^2 = R^5 = R^6 = Me$; $X = ClO_4$, $MeSO_4$.

Hydrothiolysis. The hydrothiolysis of enaminoimines was first described in relation to the reaction of a 3-ethyl-2-[2-(*N*-methyl-*N*-phenylamino)vinyl]benzothiazolium salt (CIII) with sodium hydrogen sulphide in methanol, which led to a satisfactory yield of the enaminothial (CIV):[29]



(CIII) (CIV)

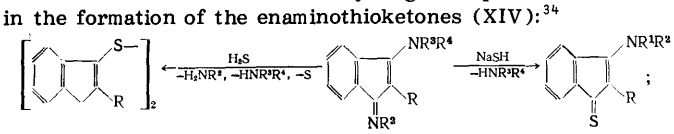
The hydrothiolysis of 3-piperidinocyclohex-2-ene-1-iminium salts (XXIX) does not proceed unambiguously. Their C(1) and C(3) atoms have similar reactivity indices,[23] which is apparently the cause of the simultaneous formation of the two enaminothioketones (XXXII) and (XXXIIa):



(XXIX) (XXXII) (XXXII a)

$R^1R^2 = (CH_2)_5$; $R^3 = H$; $R^4 = CH_2Ph$, Ph, 4-$MeOC_6H_4$.

The reactions of 3-amino-2-phenylindene-1-imines (CV) with hydrogen sulphide in the presence of piperidine lead to a reduction product—bis(indenyl)disulphide (XXXV), while the reactions with sodium hydrogen sulphide result in the formation of the enaminothioketones (XIV):[34]



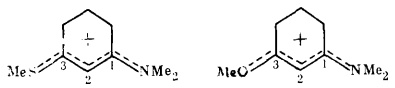
(XXXV) (CV) (XIV)

R = Ph, $R^1 = H$.

VI. QUANTUM-CHEMICAL ANALYSIS OF NUCLEOPHILIC SUBSTITUTION IN 3-ALKOXY- AND 3-ALKYLTHIO-CYCLOHEX-2-ENE-1-IMINIUM SALTS

Calculations have been carried out for the 3-methylthio- (A) and 3-methoxycyclohex-2-ene-1-*NN*-dimethyliminium (B) cations by the CNDO/2 method using a novel parametrisation.[6] The results of the calculation, which are presented solely for the chemically reactive $X-C=C-C=\overset{+}{N}Me_2$ fragment, are indicated in the molecular diagrams (A) and (B) (see Table) [the initial location of the positive charge on the N atom in the cations (A) and (B) is energetically more favourable to the extent of ~2 eV than its location on the O or S atoms]. Analysis of the molecular diagrams showed that both "soft" and "hard" nucleophiles attack the $C=\overset{+}{N}$ bond preferentially in the 3-methylthio-substituted cation (A)—this reaction pathway is subject to orbital and charge control.

Results of the calculations for the 3-methylthio- (A) and 3-methoxy-cyclohex-2-ene-1-*NN*-dimethyliminium (B) cations.



(A) (B)

Atom or bond	Form (A)			Form (B)		
	q_i, e	k_i	w	q_i, e	k_i	w
N	−0.063	—	—	−0.071	—	—
C(1)	0.275	0.36	—	0.280	0.42	—
C(2)	−0.104	—	—	−0.191	—	—
C(3)	0.211	0.26	—	0.312	0.25	—
S	0.021	—	—	—	—	—
O	—	—	—	−0.182	—	—
$C(1)=\overset{+}{N}$	—	—	1.560	—	—	1.518
C(1)=C(2)	—	—	1.420	—	—	1.452
C(2)=C(3)	—	—	1.642	—	—	1.588
C(3)—S	—	—	1.071	—	—	—
C(3)—O	—	—	—	—	—	1.147

Notation: q_i are the atomic charges, k_i are the relative contributions of the atomic π orbitals of the lowest unoccupied molecular orbital, and w are the Wiberg bond indices.

In the case of the 3-methoxy-substituted cation (B), "soft" nucleophiles should react preferentially via the $C=\overset{+}{N}$ bond (orbital control predominates), while "hard" nucleophiles should react via the C—O bond (charge control predominates), which can be accounted for by the greater electronegativity of the MeO group compared with MeS.

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Thus the problem of the analysis of the reactions considered here is fairly complex, since the aim of the majority of the published studies (which have been very numerous—cf. Hünig[80]) was not a specific investigation of the reactions of unsaturated iminium salts with nucleophiles under comparable conditions. Instances of the hydrolysis, aminolysis, and hydrothiolysis of such salts at the C(1) atom as well as the C(3) atom or at both electrophilic centres are known. It is sometimes difficult to arrive at a correct conclusion about the course of the process owing to the hydrolysis of the final product and the occurrence of other side reactions. However, the practical usefulness of further more extensive investigation of nucleophilic substitution in iminium salts has been demonstrated by recent studies,[6,81] which indicated ways of synthesising new thio-derivatives of cyclohexene and indene on the basis of these reactions.

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