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The vinyl ethers of aminoalcohols and their derivatives

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Abstract. The results of studies on the methods of synthesis and properties of the vinyl ethers of aminoalcohols are surveyed and described systematically. Their practical applications are considered. The bibliography includes 265 references.

I. Introduction

The vinyl ethers of aminoalcohols (VE AA) occupy a notable place among the vinyl derivatives of nitrogen- and oxygen-containing compounds which are widely used in organic synthesis.

By virtue of the presence of amino- and vinyloxy-groups, these compounds combine the very extensive synthetic possibilities of both amines and vinyl ethers. Here one should note that, although these groups do not exert a mutual influence on one another in the classical sense of this concept, nevertheless in many reactions the VE AA behave differently from both amines and the vinyl ethers of alcohols. This difference is manifested primarily by the competition between the amino- and vinyloxy-groups in reactions with electrophiles and also by the occurrence of secondary processes with participation of the group which is not involved in the main reaction.

As a result of the lower dissociation energy of the C–N bond compared with the C–O and C–C bonds, the conditions in the main method for synthesis of vinyl ethers — vinylation of alcohols by ethyne — frequently prove to be somewhat too severe for the vinylation of aminoalcohols and leads to the elimination of the amino-group. Furthermore, the reaction is complicated by *N*-vinylation and cyclisation processes.

Thus specific methods, differing significantly from those known for aliphatic amines and vinyl ethers, are frequently needed to increase the selectivity and yields both in the synthesis of the VE AA and in their chemical reactions.

Individual questions associated with the synthesis and chemical properties of the VE AA have been considered hitherto in monographs[1–5] and reviews[6–8] devoted to the chemistry of ethyne and its derivatives. However, the range of problems discussed there is extremely narrow because of the specific nature of the publications and, furthermore, these compounds are considered mainly as a special case of the vinyl ethers of alcohols.

In the present review, an attempt is made to represent as fully as possible the available literature data on the synthesis and chemical properties of the VE AA, the aim being also to demonstrate and assess the position occupied by these compounds in organic synthesis. The prospects for their practical application are also considered.

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II. Methods of synthesis of the vinyl ethers of aminoalcohols

1. Interaction of aminoalcohols with ethyne

Among the methods of synthesis of the VE AA known hitherto, the commonest and most universal is the base-catalysed addition of aminoalcohols to ethyne.

$$RR^1NCR^2R^3(CH_2)_nCR^4R^5OH \xrightarrow{CH\equiv CH} RR^1NCR^2R^3(CH_2)_nCR^4R^5OCH{=}CH_2$$

$n = 0–8$; $R–R^5$ = H, Alk, Ar, Het;

R = $Me_3Si(CH_2)_3$, CH_2CH_2OH, $CH_2CH_2NH_2$;

$R + R^1 = -CH_2CH_2OCH_2CH_2-$;

$R + R^1$, $R + R^2$, $R + R^4$, $R^2 + R^4 = -(CH_2)_{2-5}-$.

Since the 1930's, this reaction has been used to obtain a wide range of VE AA with various structures.[9–50]

The potassium or sodium alkoxides derived from the aminoalcohols to be vinylated[9–29] or the hydroxides of the corresponding metals were used (in an amount corresponding to 5%–20% of the weight of the aminoalcohol) as the catalyst.

Lithium, sodium, potassium, rubidium, and caesium oxides, hydroxides, alkoxides, phenoxides, naphthoxides, cyanides, zincates, and sulfides have been proposed as the catalysts in a series of patents.[30–32]

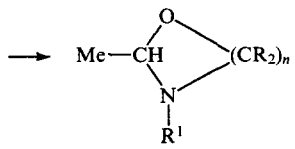
The interaction of the aminoalcohols **1** with ethyne in the absence of catalysts[9,51,52] and also in the reaction catalysed by cadmium acetate[33,53] results in the formation either of polymerisation products[9,53] or of 2-methyl-1,3-oxazacycloalkanes **2**.[33,51,52]

It has been suggested that the formation of the cyclic product **2** is associated with the occurrence under these conditions of the *N*-vinylation and subsequent cyclisation of the unstable intermediate enamines.[51] It is noteworthy that the *N*-vinylation, especially in the case of aminoalcohols with a secondary

hydroxy-group which is difficult to vinylate, is possible also under the conditions of base catalysis. Thus it has been reported that only 3-aryl-5-aryloxymethyl-2-methyl-1,3-oxazolidines were obtained from 3-arylamino-1-aryloxypropan-2-ols and ethyne.[54]

$$HO(CR_2)_nNHR^1 \xrightarrow[100-200\,^\circ C]{CH\equiv CH,\ 2-4\ MPa}$$

1 (conversion 10% – 30%)



2 5% – 75%

n = 2, 3; R = H, Me, Et;

R^1 = H, Me, Ph, CHMePh, CH_2CH_2OH, $CH_2CH_2NH_2$.

The vinylation of aminoalcohols at atmospheric pressure of ethyne is usually carried out without solvents.[10-17,34-36] On the other hand, when the reaction is carried out in autoclaves, solvents are usually employed, for example benzene,[9,18-26,37] dioxane,[21,38,39] *tert*-butyl alcohol,[27] n-butyl alcohol,[33] ethers and polyethers,[30] and dimethyl sulfoxide.[40] This greatly increases the amount of ethyne introduced into the reaction, accelerates the process, and makes it possible to raise the yield of the products. The use of water as the solvent lowers the yield of the products and hinders their isolation.[9,22]

The reaction temperature and ethyne pressure are varied within wide limits depending on the structure of the aminoalcohol and the method used for carrying out the reaction. Thus the vinylation of ethanolamines in the vapour phase,[31,32,41] (temperature 250 – 300 °C) and in a gas – liquid emulsion[10,12-14,16,17] in flow-type[11,36] and bubble-type[34,35] reactors has been carried out at atmospheric pressure (temperature 100 – 150 °C, yield of the VE AA 54% – 86%), while the reaction in the liquid phase[30] has been performed at 11.2 MPa and a temperature of 120 – 180 °C with a yield of 75% – 95%. In the vinylation in periodic-action autoclaves, which is commonest, the initial ethyne pressure is usually 1 – 2.5 MPa and the temperature is 100 – 180 °C.

A detailed analysis of various methods for the vinylation of ethanolamines and an assessment of the prospects for their industrial application on the basis of literature data published up to 1972 have been presented in a monograph.[2] The monograph deals with problems concerning the optimisation of the process and its kinetics and discusses the ways in which the side products of the reaction are formed and the methods for the analytical monitoring, isolation, and purification of the vinyl ethers.

From the standpoint of practical application, the vinyl ether of monoethanolamine **3** is undoubtedly of greatest interest. However, in the series of ethanolamines the vinylation of monoethanolamine actually involves the greatest difficulties.[9,11,23] It has been shown recently that the main reason for this is the ready decomposition at a temperature above 100 °C of the ether **3** by alkali.[55,56] In the presence of potassium hydroxide at 110 – 115 °C, it decomposed to the extent of 70% after 5 h, affording a 45% yield of the azomethine **4** and other extensive degradation products. Under the same conditions but in the presence of sodium hydroxide, the degree of decomposition of the ether **3** did not exceed 2%.

In this connection, it is clear that, in the synthesis of the vinyl ether **3**, its continuous removal from the reaction zone is necessary and that preference should be given to sodium hydroxide as the catalyst. Taking into account these refinements, a method has been developed for the vinylation of monoethanolamine at atmospheric pressure in which the yield of the ether **3** is 93% – 96%.[53,57]

$$CH_2{=}CHOCH_2CH_2NH_2 \xrightarrow{MOH}$$

3

$$\longrightarrow CH_2{=}CHOCH_2CH_2N{=}CHCH_3 + NH_3$$

4

$$+H_2 + H_2O + EtOH + MeCOOM + M_2CO_3$$

M = K, Na.

2. Interaction of aminoalcohols with substituted ethynes

There are very few literature data on the synthesis of VE AA having substituents in the vinyl group by the addition of aminoalcohols to substituted ethynes.

It has been shown that the addition of one molecule of 2-diethylaminoethanol to diethyne in the 1,2-positions with formation of the *cis*-isomer **5** takes place exothermically without catalysts. The addition of a second molecule requires a catalyst (potassium alkoxide or hydroxide) and heating. This results in the formation of both regioisomers **6** and **7** in an overall yield of 55% – 60%.[25,58-60]

$$CH{\equiv}C{-}C{\equiv}CH \xrightarrow{Et_2N(CH_2)_2OH}$$

$$\longrightarrow Et_2N(CH_2)_2OCH{=}CH{-}C{\equiv}CH \xrightarrow{Et_2N(CH_2)_2OH}$$

5 80% – 90%

$$\longrightarrow Et_2N(CH_2)_2OCH{=}CH{-}\underset{\displaystyle O(CH_2)_2NEt_2}{\underset{|}{C}}{=}CH_2 +$$

6

$$+\ Et_2N(CH_2)_2OCH{=}CH{-}CH{=}CHO(CH_2)_2NEt_2$$

7

The study of the reactions of diethyne alcohols **8** with aminoalcohols established that, at 105 – 110 °C in the presence of potassium hydroxide, acetone is split off from the alcohols **8** and the resulting diethynes **9** combine with aminoalcohols, affording the vinylethyne derivatives **10** in yields up to 52%.[61]

$$R{-}C{\equiv}C{-}C{\equiv}C{-}CMe_2OH \xrightarrow[-Me_2CO]{}$$

8

$$\longrightarrow R{-}C{\equiv}C{-}C{\equiv}CH \xrightarrow{HO(CH_2)_2NR^1_2}$$

9

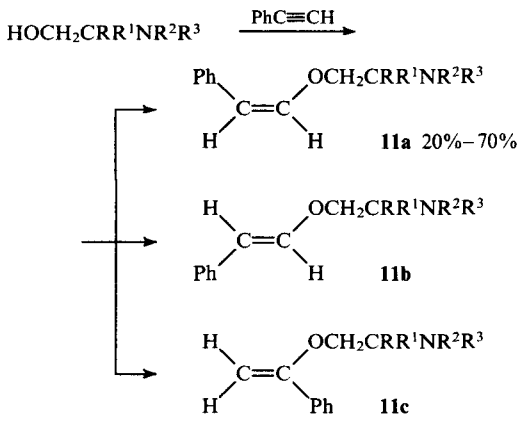
$$\longrightarrow R{-}C{\equiv}C{-}CH{=}CHO(CH_2)_2NR^1_2$$

10

R = Me, Ph; R^1 = Et, Bu.

The use of diethyne as well as other substituted ethynes with an activated triple bond is probably limited to the synthesis of vinyl ethers with a tertiary amino-group, since aminoalcohols with primary or secondary amino-groups add to such ethynes as typical amines with formation of enamines.[62-64]

The study of the reactions of aminoalcohols with phenylethyne showed that, at 120 – 130 °C in the absence of solvents, the products **11a** of the *trans*-addition to the β-carbon atom in phenylethyne are formed preferentially on treatment with alkali metal hydroxides. The amount of the products **11b** of the *cis*-addition is between 3% and 15%, while that of the products **11c** of the addition to the α-carbon atom in phenylethyne is 2% – 5% relative to the amount of the *trans*-isomer **11a**. When the reaction is carried out in dimethyl sulfoxide (DMSO), its stereoselectivity diminishes (the ratio of the *trans*- and *cis*-adducts **11a** and **11b** is 1:0.6), but their regiospecificity is unaffected.[65,66]

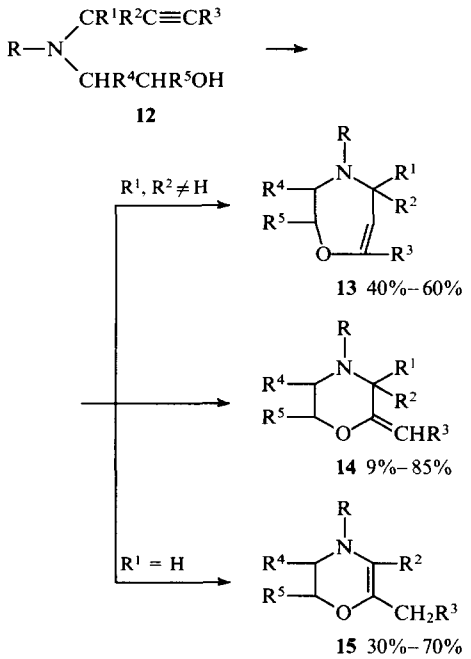


R, R^1 = H, Me, Et; $R^2+R^3 = -CH_2CH_2OCH_2CH_2-$;

R^2, R^3 = H, Me, Et, CH_2Ph, Ph, 2-MeC_6H_4, 4-MeC_6H_4, Ac.

The base (KOH, $NaNH_2$)-catalysed intramolecular cyclisation of *N*-propargylethanolamines **12** to the oxazepines **13**[67,68] or the morpholine derivatives **14** and **15** (Scheme 1)[1,39,69–72] is a special case of the reaction under consideration.

Scheme 1



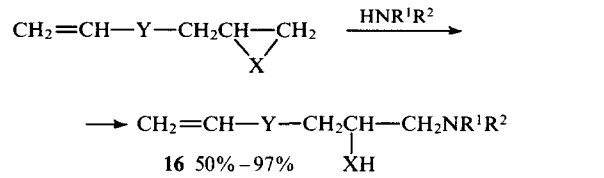
R = H, Me, Et, Bu^t, CH_2CH_2OH; $R^1 = R^2 = H$, Me;

$R^1+R^2 = -(CH_2)_5-$;

R^3, R^4, R^5 = H, Me, $CH_2CH=CH_2$, Ph, $PhCH_2CH_2$, 2-$MeOC_6H_4$, 4-$MeOC_6H_4$, CH_2OMe, $CH_2OCH=CH_2$, CH_2NEt_2.

3. Other methods of synthesis of the vinyl ethers of aminoalcohols

A series of procedures for the synthesis of VE AA based on the reactions of amines with reactants containing the vinyl group have been described. For example, the vinyl ethers **16** have been obtained by the reaction of amines with the vinyl derivatives of oxiranes[73–79] and thiiranes.[80]

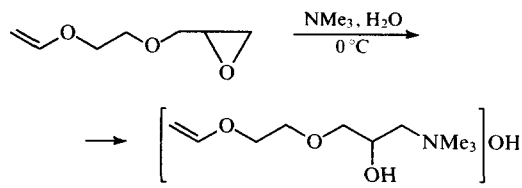


X = O, S; Y = O, $O(CH_2)_2O$, $O(CH_2)_3O$, $OCHMeCH_2CH_2O$, $O(CH_2)_2O(CH_2)_2O$, $O(CH_2)_2O(CH_2)_2O(CH_2)_2O$;

R^1, R^2 = H, Et, Pr, Bu, Bu^t, $CH_2CH=CH_2$, CH_2Ph, CH_2CH_2OH, $CH_2CH(OH)CH_2OCH_2CH_2OCH=CH_2$;

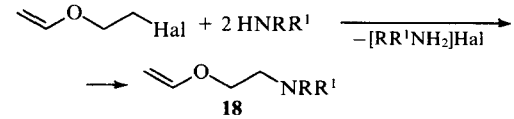
$R^1+R^2 = -(CH_2)_5-$, $-CH_2CH_2OCH_2CH_2-$.

The quaternary base **17** has been obtained from trimethylamine and the glycidyl vinyl ether of ethylene glycol.[75]



17 83%

Methods have been developed for the synthesis of the vinyl ethers of the aminoethanols **18**[18,81–84] and their quaternary salts **19**[85] by the nucleophilic substitution of the halogen in 2-haloethyl vinyl ethers by amines.



18

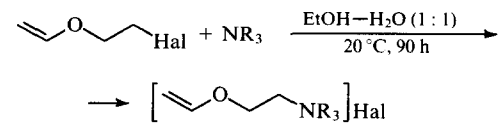
Hal = Cl, Br;

R = R^1 = Bu (30%), $CH_2CH=CH_2$ (26%), $CH_2=C(Me)CH_2$ (29%);

R = H, R^1 = CH_2Ph (61%); R = H, R^1 = $Me_3Si(CH_2)_3$ (70%);

R = Bu, R^1 = $CH_2CH=CH_2$ (57%);

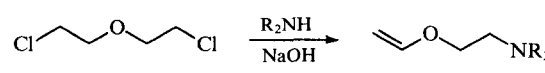
$R+R^1 = -(CH_2)_5-$ (55%), $-CH_2CH_2OCH_2CH_2-$ (90%).



19

Hal = Br, R = Me (82%); Hal = I, R = Me (67%).

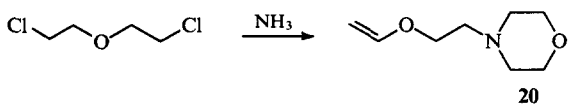
The vinyl ethers of aminoalcohols have also been obtained by the reaction of secondary aliphatic and aromatic amines with di(2-chloroethyl) ether at 50–200 °C with subsequent treatment of the reaction mixture with an aqueous solution of sodium hydroxide.[86]



R = Et, Bu, C_6H_{13};

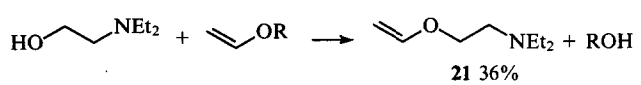
R_2 = $-(CH_2)_5-$, $-CH_2CH_2OCH_2CH_2-$, $-CH=CH-CH=CH-$

The vinyl ether of 2-morpholinylethanol **20** has been obtained from an aqueous solution of ammonia and di(2-chloroethyl)ether under similar conditions.[87]



20

Attempts have been made to synthesise VE AA by the mercury acetate-catalysed transvinylation reaction. It was then possible to obtain only the vinyl ether of 2-diethylaminoethanol **21**.[88]



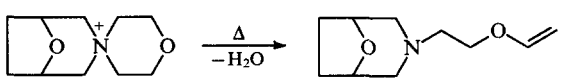
21 36%

R = Et, CH_2CH_2OBu.

Only 2-methyl-1,3-oxazacycloalkanes **2** have been obtained from the amino-alcohols **1** with primary and secondary aminogroups under the conditions of this reaction.[89,90]

The addition of amines,[91–94] alcohols,[93,95] thioalcohols,[93,96] urea,[97] and carboxylic acids[98] to 2-vinyloxyalkyl isocyanates[94,97] and to 2-vinyloxyethyl isothiocyanate (Scheme 2) may be regarded as a method of synthesis of the vinyl ethers of *N*-acyl- and *N*-thioacyl-ethanolamines.

The Hofmann degradation of the morpholine bases can also lead to vinyl ethers. However, the only example is the synthesis of the vinyl ether **23** from the spirocyclic morpholine base **22**.[99]



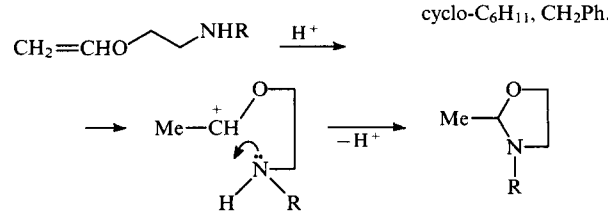
22 **23** 57%

III. Chemical properties of the vinyl ethers of aminoalcohols

1. Reactions of the vinyl ethers of aminoalcohols with acids

In contrast to aliphatic amines, the VE AA contain several basicity centres of different nature: hard centres (nitrogen and oxygen atoms) and a soft centre (the sp^2-carbon atom). This is the reason for their more complex, compared with aliphatic amines, behaviour in relation to acids. Thus, there is only isolated evidence that the salts of vinyloxyethylamines and protic acids, for example the substituted benzoates[100] and the oleate[101] of the amine **3**, as well as the picrates of *N*,*N*-bis(2-vinyloxyethyl)-amines[102] and vinyloxyethylmorpholine **23**[99] can be obtained in solution in benzene.

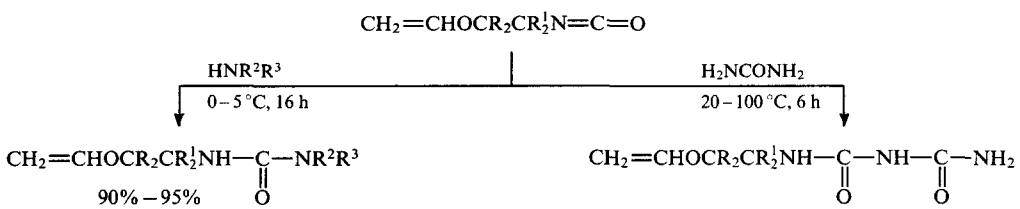
As a result of the reduction of the basicity of the nitrogen atom due to the electronic effect of the substituents, the protonation of the soft basicity centre becomes competitive. Thus the vinyl ether of *N*-phenylethanolamine is cleaved by traces of hydrochloric acid to phenylaminoethanol and products of unknown structure. At the same time, it cyclises to 2-methyl-3-phenyloxazolidine in 13% yield.[22] The even more weakly basic vinyl ethers of *N*-acylethanolamines cyclise quantitatively[91,103–107] in the presence of catalytic amounts of protic acids.



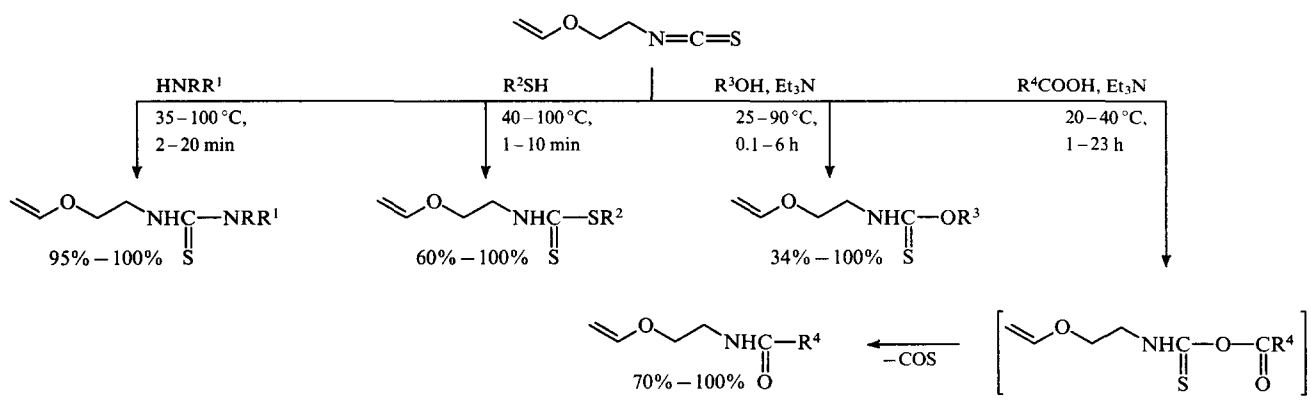
R = Ph (13%), Ac (100%), C(S)SAlk (100%),

Alk = Me, Et, Pr, Bu, Bu^i, Bu^t, $CH_2CH{=}CH_2$, cyclo-C_6H_{11}, CH_2Ph

Scheme 2



R, R^1, R^2, R^3 = H, Me, Et, C_8H_{17}, $C_{12}H_{25}$.



R, R^1 = H, Me, Et, Bu, Bu^i, $CH_2CH{=}CH_2$, cyclo-C_6H_{11}, CH_2CH_2OH, CH_2CH_2SH, $CH_2CH_2OCH_2CH_2SBu$, Ph, 2,4-$Me_2C_6H_3$, 3,4-$Cl_2C_6H_3$, 3-ClC_6H_4, 2-$MeCOC_6H_4$, 2-$C_{10}H_7$, 3-Me-2-C_5H_3N;

R+R^1 = $-(CH_2)_5-$, $-CH_2CH_2OCH_2CH_2-$; R^2 = Et, Pr, Bu, C_5H_{11}, C_6H_{13}, C_7H_{15}, CH_2Ph;

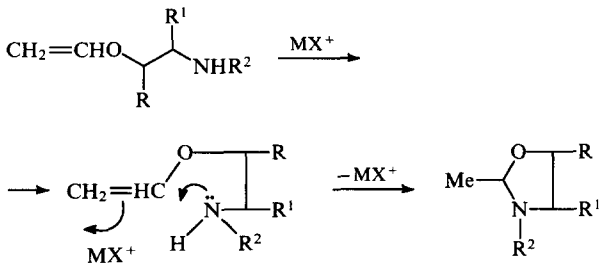
R^3 = $CH_2(CF_2)_nH$, n = 2, 4, 6, 8, 10; R^4 = Me, Et, Pr^i, Bu, Bu^i, C_7H_{15}, Ph, (3-Ind)CH_2 (Ind = indolyl).

When cyclisation is impossible due to structural factors, as happens, for example, in the case of the weakly basic vinyl ether of *N,N*-diphenylethanolamine[19] or quaternary vinyloxyethylammonium salts,[83] polymerisation involving the vinyl group, catalysed by strong acids (H^+, Fe^{3+}, BF_3), takes place readily.

The highly basic vinyl ethers, for example the vinyl ethers of *N*-monoalkylethanolamines and *N,N*-dialkylethanolamines, as well as the vinyl ethers **16** (X = O) neither cyclise nor polymerise on treatment with catalytic amounts of HCl, $FeCl_3$, and $BF_3.Et_2O$.[19,22,26,75]

However, on treatment with more than an equimolar amount of BF_3 [108,109] or $BF_3.Et_2O$, [40] the VE AA polymerise regardless of the structure of the amino-group, since in this case the complex of the vinyl ether with BF_3 actually polymerises and not the ether itself.

Soft acids (for example, Hg^{2+} and Pd^{2+}) coordinating to the soft π-basic centre induce the cyclisation of the VE AA regardless of the basicity of their amino-group.[110–112]



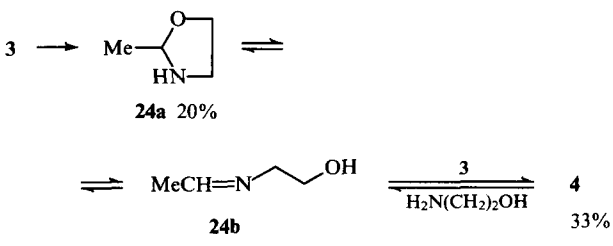
76%–99%

R, R^1 = H, Me, $MeOCH_2$;

R^2 = H, Me, Et, CH_2Ph, Ph, Ac, CH_2CH_2OH, CH_2CH_2CN, $CH_2CH_2OCH{=}CH_2$;

M = Hg, Pd; X = Cl, AcO.

The reaction is complicated by the occurrence of an exchange process with formation of the azomethine **4** only in the case of the simplest vinyl ether **3** owing to the ability of the oxazolidine **24a** to undergo a tautomeric transformation into the azomethine alcohol **24b**.



24a 20%

24b

33%

The available data on the interaction of VE AA with acids belonging to the class intermediate between hard and soft acids are limited to only one example of the formation of a chelate complex of the vinyl ether of monoethanolamine $[(CH_2{=}CHO(CH_2)_2NH_2)_2Cu]Cl_2$, in which the copper atom is coordinated simultaneously to the ether oxygen and the amino-group.[113]

2. Alkylation

The alkylation of VE AA with a tertiary amino-group usually leads to the formation of monomeric quaternary salts.[25,83,85,114–177] As in the quaternisation of aliphatic amines, in this case the yields of the salts and the reaction time depend greatly on the structure of the amino-group and of the alkylating agent and also on the reaction conditions. For example, in the interaction of the vinyl ether of diethylaminoethanol with ethyl bromide in the absence of a solvent at 20 °C, the yield of the quaternary salt is only 15% after 21 days.[116] The alkylation of 4-(2-vinyloxyethyl)-1,4-perhydrotriazine 1-oxide by benzyl chloride, allyl bromide, or methyl iodide at 20 °C in nitromethane is completed by the formation of the corresponding salts in 93%–97% yields after only 10–12 h.[115]

$$CH_2{=}CHO(CH_2)_nNRR^1 + R^2X \longrightarrow [CH_2{=}CHO(CH_2)_nNRR^1R^2]X$$

R = Bu, R^1 = $CH_2CH{=}CH_2$;

R = R^1 = Et, Bu, $CH_2CH{=}CH_2$, $CH_2C(Me){=}CH_2$;

R + R^1 = $-(CH_2)_5-$, $-CH_2CH_2OCH_2CH_2-$, $-CH_2CH_2S(O)CH_2CH_2-$;

R^2 = Me, Et, $CH_2CH{=}CH_2$, $CH_2C{\equiv}CH$, CH_2Ph, CH^2COCH_3, CH_2COPh; X = Cl, Br, I, $MeSO_4$, 4-$MeC_6H_4SO_3$.

Only polymeric quaternary salts have been obtained in the alkylation of the trivinyl ether of triethanolamine[19] and also of the vinyl ether **16** (X = O)[75] by methyl iodide. Partial polymerisation is observed when amines of the type $(CH_2{=}CHOCH_2CH_2)_2NCH_2XAlk$ (where X = O, S) are treated with alkyl halides.[102]

The alkylation of the vinyl ethers of aminoalcohols with primary[84,118] and secondary amino-groups by alkyl halides, methyl monochloroacetate,[19] and chloro- or bromo-cyanogen[119] in the presence of KOH,[38,69,84,118,120,121] NaOH,[19] Na_2CO_3,[117] and K_2CO_3,[40,119] leads to the formation of the corresponding secondary and tertiary amines in 50%–95% yields without any complications.

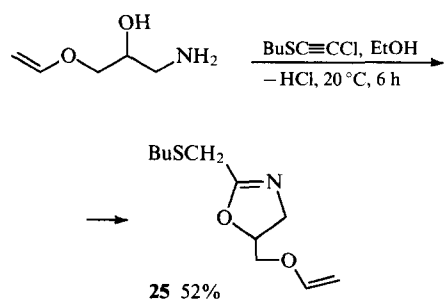
$$RNHCR^1_2CHR^2OCH{=}CH_2 + R^3Hal \longrightarrow RR^3NCR^1_2CHR^2OCH{=}CH_2$$

R = H, Me, Et, Ph, CH_2Ph, $CH_2C{\equiv}CH$, CH_2CH_2OH, $CH_2CH_2OCH{=}CH_2$

R^1, R^2 = H, Me; $RNHCR^1_2CHR^2 = \overline{CH_2CMe_2NHCMe_2CH_2CH}$;

R^3 = Me, $CH_2CH{=}CH_2$, $CH_2C{\equiv}CH$, CH_2Ph, CH_2COOMe, CH_2COOEt, CN; Hal = Cl, Br, I.

In the interaction of the monovinyl ether of 3-aminopropane-1,2-diol with butylthiochloroethyne, the hydroxyl adds to the triple bond with formation of the oxazoline **25** in addition to the chlorine-substitution reaction.[122]

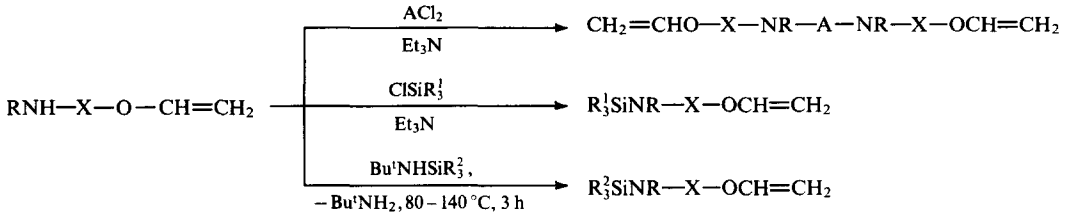


25 52%

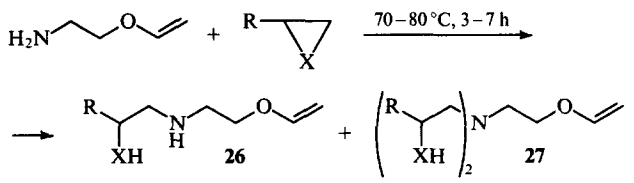
Both the products **26** and **27** with alkoxy- and alkylthio-substituents and the vinyl ethers of epoxyaminoalcohols **28** have been obtained[123] by the interaction of VE AA with epoxy-compounds[76] and thiiranes.[80]

Together with alkylation, also the silylation of VE AA, for example by α-ω-dichloropolysiloxanes,[124] alkyl(aryl)chlorosilanes, and silylamines, has been described (Scheme 3).[125]

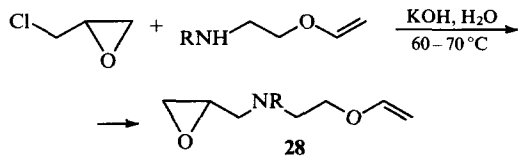
Scheme 3



X = $(CH_2)_2$, CMe_2CH_2, $CMe_2(CH_2)_3CHMeCH_2CH_2$; A = $(SiMe_2O)_nSiMe_2$; R = H, Alk; R^1 = Alk, Ph, Cl; R^2 = Alk, Ph.



X = O, S; R = $CH_2OCH_2CH_2OCH{=}CH_2$,

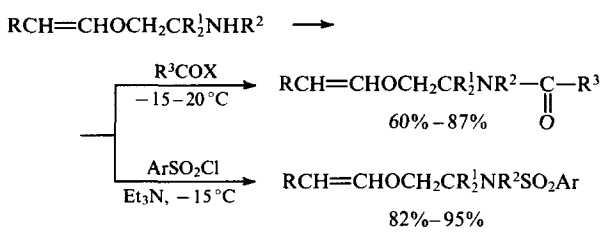


R = $CH_2CH{=}CH_2$ (82%); $CH_2CH_2OCH{=}CH_2$ (75%)

3. Acylation

The acylation of VE AA by the anhydrides[65,126,127] and chlorides of carboxylic acids[128–130] and sulfonic acids[84] usually takes place without complications of any kind.

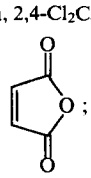
The reaction is carried out in the presence of organic bases



R = H, Ph; R^1 = H, Me;

R^2 = H, CH_2Ph, 4-$Me_2NC_6H_4CH_2$, 4-$MeOC_6H_4CH_2$, $CH_2CH_2OCH{=}CH_2$, $\overline{OCH{=}CH{-}CH{=}CCH_2}$, CH_2CH_2COOBu, $CH_2CHMeCOOMe$;

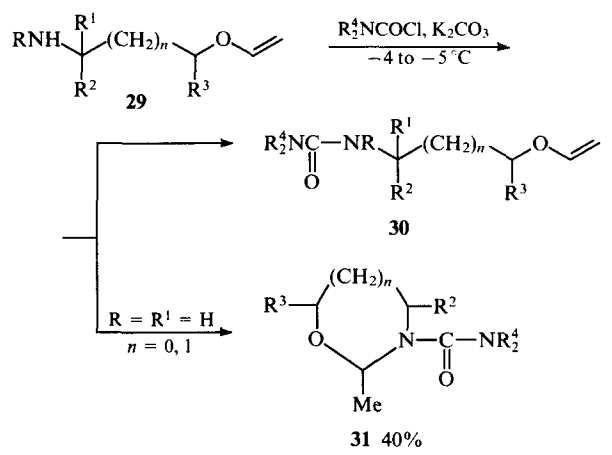
R^3 = Me, Ph, 2,4-$Cl_2C_6H_3OCH_2$, EtO; X = Cl, AcO;

R^3COX = ; Ar = Ph, 4-MeC_6H_4.

(pyridine,[128] triethylamine[84,129]) or inorganic bases[65] as acid acceptors. An excess of the vinyloxyalkylamine is more rarely employed.[127,130]

Both linear carbamides **30**[94] and cyclic carbamides **31**[131] have been obtained as a result of the acylation of the VE AA **29** by *N,N*-dialkylcarbamoyl chlorides.

The carbamides **30** are formed from the amines **29** with a secondary amino-group and also from the same amines with a primary amino-group, for which there is steric hindrance to cyclisation ($n > 2$ or the amino-group is attached to a tertiary carbon atom). Only the carbamides **31** have been obtained in all other cases.



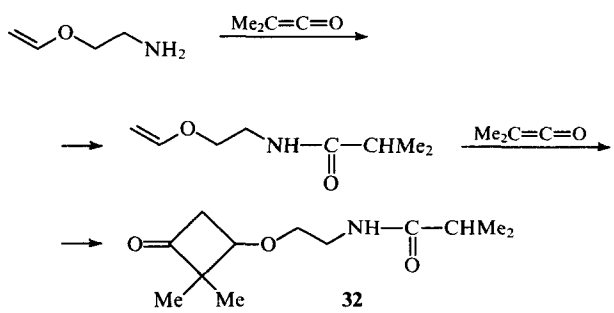
n = 0–3, 4, 8;

R, R^1, R^2, R^3 = H, Me, Bu, $C_{12}H_{25}$, $C_{18}H_{37}$, CH_2Ph, cyclo-C_6H_{11};

R^4 = Me, Et, Bu, $C_{12}H_{25}$, $C_{18}H_{37}$, cyclo-C_6H_{11};

R^4_2 = $-(CH_2)_5-$, $-CH_2CH_2OCH_2CH_2-$.

In the interaction of diethylketene with the vinyl ether of monoethanolamine, the latter is initially acylated, after which cycloaddition takes place and leads to the formation of the cyclobutanone **32** in 80% yield.[132]



The acylation of VE AA by esters is carried out by keeping the reactant mixture for 2–7 days at room temperature or for 5–40 h at 60–95 °C.[18,97,133,134]

$$RNH(CH_2)_nOCH{=}CH_2 \xrightarrow[-R^2OH]{R^1COOR^2} \rightarrow R^1CONR(CH_2)_nOCH{=}CH_2$$

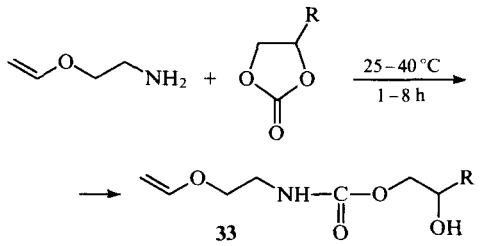
30%–75%

R = H, Me, Ph, CH_2Ph, $CH_2CH_2OCH{=}CH_2$, $Et_3Si(CH_2)_3$;

R^1 = Me, CH_2OH, CH(OH)Me, $CH_3(CH_2)_5CH(OH)CH_2CH{=}CH(CH_2)_7$, $NH_2C(O)NH$;

R^2 = Me, $CH{=}CH_2$; n = 2, 3.

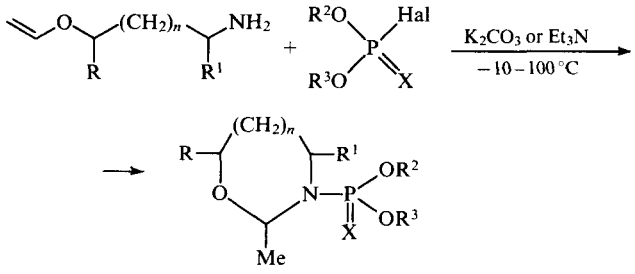
Cyclic carbonates interact with vinyloxyethylamine much more readily, affording high yields of the carbamates **33**.[135–138]



33

R = H (70%), CH_2Cl (100%).

The reactions of dialkyl phosphorothiohalidates or phosphorohalidates with the vinyl ethers of ethanol- and propanolamines lead to the cyclic phosphoramidate derivatives **34**.[139]

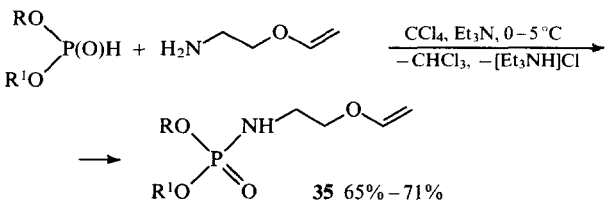


34 70%–80%

n = 0, 1; R = H, Me, $C_{16}H_{33}$, Ph; R^1 = H; X = O, S;

$R^2 = R^3$ = Et, $C_{12}H_{25}$, Ph; $R^2 + R^3 = -(CH_2)_2-$; Hal = F, Cl, Br.

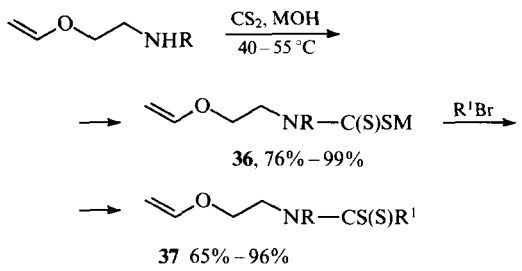
The acyclic phosphoramidates **35** have been obtained by the reaction of dialkyl phosphites with the vinyl ether of monoethanolamine in the presence of carbon tetrachloride and triethylamine.[140]



35 65%–71%

R, R^1 = Et, Pr, Pr^i, Bu, Bu^i, C_5H_{11}.

The dithiocarbamic acid salts **36** have been obtained by the reaction of the vinyl ethers of mono- and di-ethanolamines with carbon disulfide in the presence of alkali metal hydroxides.[141–143] Subsequent alkylation of the salts gave rise to the dithiocarbamates **37**.[141,144]



36, 76%–99%

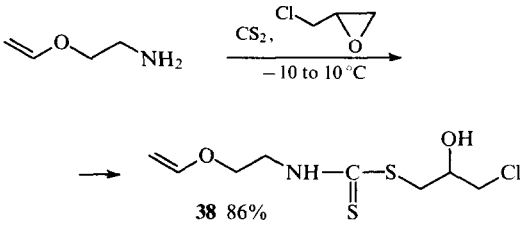
37 65%–96%

R = H, $CH_2CH_2OCH{=}CH_2$;

R^1 = Me, Et, Bu, Bu^i, CH_2Ph, $CH_2CH{=}CH_2$, $CH_2C{\equiv}CH$;

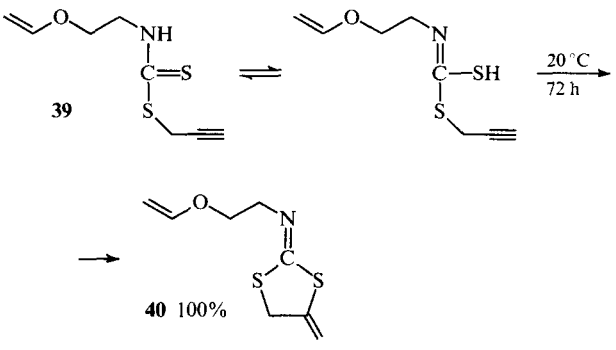
M = Na, K.

The joint treatment of 2-vinyloxyethylamine with carbon disulfide and epichlorohydrin leads to the dithiocarbamate **38**.[145]



38 86%

The thione–thiol tautomerism of dithiocarbamates leads to the possibility of the existence of derivatives of the isomeric dithiocarbamic acid. This type of cyclic derivative **40** has been obtained from the dithiocarbamate **39** at room temperature in a quantitative yield.[144]



40 100%

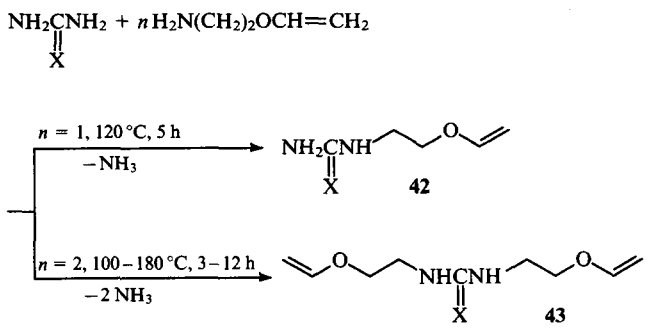
Carbon dioxide and carbon disulfide react readily with VE AA, but the stable carbamic acid salts **41** have been obtained only for the vinyl ethers of 2-amino-ethanol and 3-aminopropanol.[146]

$$2\,CH_2{=}CHO(CH_2)_nNH_2 \xrightarrow{CO_2} [CH_2{=}CHO(CH_2)_nNHC(O)O]NH_3(CH_2)_nOCH{=}CH_2$$

41 99%

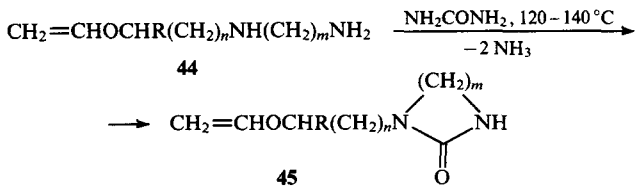
n = 2, 3.

The amide exchange reaction has also been used to acylate vinyloxyalkylamines. For example, when urea or thiourea is fused together with the vinyl ether of ethanolamine high yields of *N*-mono(2-vinyloxyethyl)urea and *N,N*-bis(2-vinyloxyethyl)-urea, as well as the corresponding thiourea derivatives (compounds **42** and **43**) were obtained depending on the reactant ratio.[42,147]



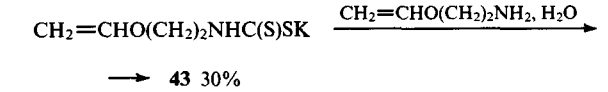
X = O, S.

The cyclic ureas **45** have been obtained from the vinyl ethers **44** and urea under similar conditions.[43]



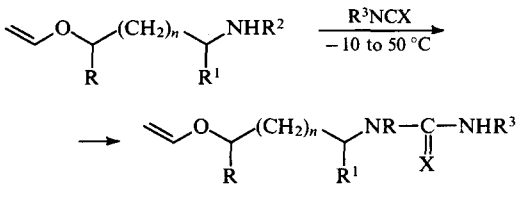
n = 1, 2; m = 2, 3; R = H, cyclo-C_6H_{11}, Ph.

The substituted thiourea **43** has also been synthesised by the interaction of an aqueous solution of a potassium carbamate derivative with vinyloxyethylamine.[148]



Isocyanates,[84,94,129,149,150] isothiocyanates,[91,150–152] and isocyanic acid, obtained in situ from KOCN and inorganic acids at pH 6.8,[153,154] readily combine with vinyloxyalkylamines, giving rise to the corresponding urea and thiourea derivatives **46** (Scheme 4).

Scheme 4



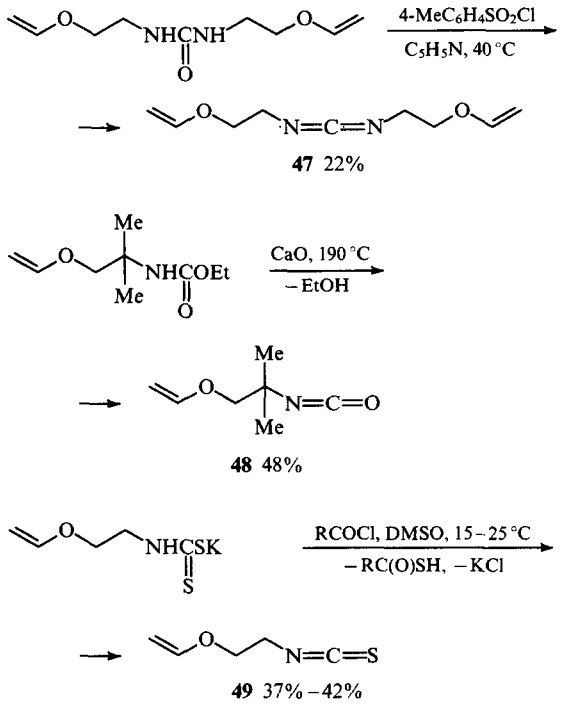
n = 2–5; R, R^1 = Me, Et, $C_{16}H_{33}$, Ph;

R^2 = H, Me, Et, Bu, cyclo-C_6H_{11}, CH_2Ph, $CH_2CH_2OCH{=}CH_2$, CH_2CH_2CN, 4-$Me_2NC_6H_3CH_2$, 4-$MeOC_6H_4CH_2$, $\overline{OCH{=}CH{-}CH{=}C}CH_2$, CMe=CHC(O)Me, $\overline{CH_2CH_2OCHMeCH}$, $\overline{CH_2(CH_2)_3CHMeCH}$;

R^3 = H, Me, Et, Bu, $MeOCH_2$, $BuOCH_2$, Ph, 2-ClC_6H_4; X = O, S.

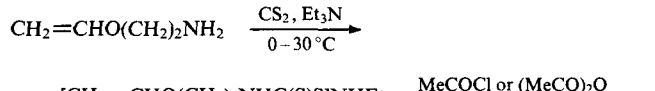
Some of the vinyl derivatives of urea and carbamic and dithiocarbamic acids described above have been used to synthesise vinyl-containing carbodiimide (compound **47**),[155] isocyanate (compound **48**),[130] and isothiocyanate (compound **49**)[104,106,156] derivatives (Scheme 5).

Scheme 5



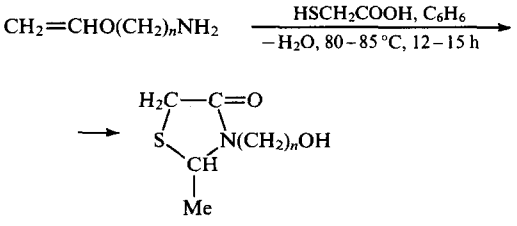
R = Me, Ph.

It was shown that the method of synthesis of the isothiocyanates **49** can be greatly improved by combining the synthesis of the carbamic acid salt from vinyloxyethylamine and carbon disulfide with the subsequent treatment with acid anhydrides. This single-reactor synthesis makes it possible to raise the yield of the isothiocyanate **49** to 95%.[157,158]



The replacement of carboxylic acid anhydrides by $POCl_3$ lowers the yield of compound **49** to 21%.[159]

Carboxylic acids are unsuitable for the acylation of VE AA owing to the instability of the latter in an acid medium already mentioned. The not altogether unusual result of the reactions of vinyloxyethyl- and vinyloxypropyl-amines with thioglycolic acid may serve as confirmation of this.[160]

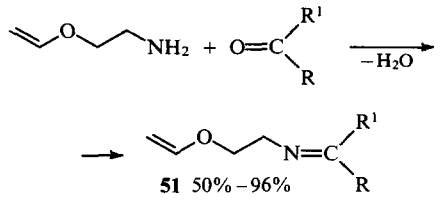


n = 2, 3.

Here there is also a possibility of the intermediate formation of the azomethine alcohol **24b**, which subsequently reacts with thioglycolic acid, affording the thiazolidinone **50**.[161]

4. Reactions with carbonyl compounds

As a typical primary amine, the vinyl ether of monoethanolamine readily condenses with aldehydes[162–164] and ketones,[165–169] giving rise to the Schiff bases **51**.

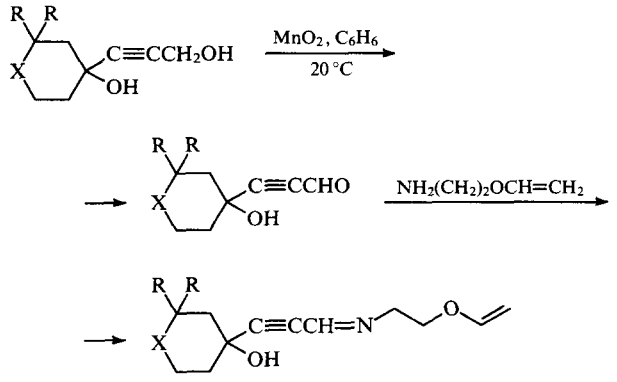


51 50%–96%

R, R^1 = H, Me, Ph, 2-HOC$_6$H$_4$, 4-MeOC$_6$H$_4$, 4-NO$_2$C$_6$H$_4$, 3-NO$_2$C$_6$H$_4$, 4-ClC$_6$H$_4$, 3-CF$_3$C$_6$H$_4$, 4-Me$_2$NC$_6$H$_4$, 3,4-(MeO)$_2$C$_6$H$_3$, OCH=CH–CH=C;

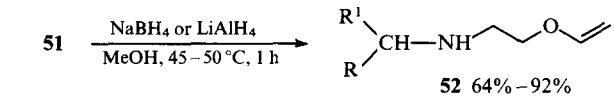
R + R^1 = –(CH$_2$)$_{4-5}$–, –CHMe(CH$_2$)$_4$–, –CHMeCH$_2$NMeCHMeCH$_2$–, –CH$_2$CH$_2$OCMe$_2$CH$_2$–.

The condensation of the vinyl ether of monoethanolamine with aldehydes proceeds so smoothly that it is possible to obtain the Schiff bases of unstable ethynealdehydes by oxidising ethyne glycols with active manganese dioxide in the presence of the above amine.[170,171]



X = O, R = Me (49%); X = CH$_2$, R = H (61%).

The hydrogenation of the vinyl derivatives of Schiff bases by hydrogen on Raney nickel even at room temperature and atmospheric pressure proceeds with reduction of the C=N and C=C bonds.[162] The selective reduction of the C=N bond alone with formation of the ether **52** is achieved with the aid of metal hydrides.[84,121,166–169]

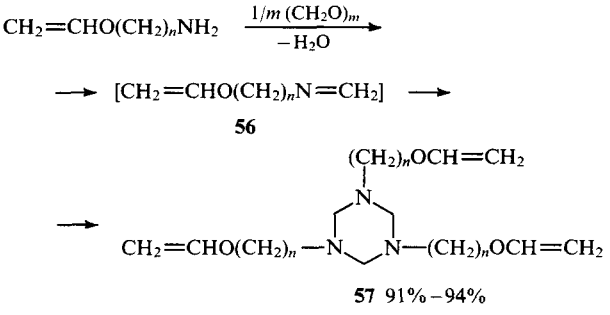


52 64%–92%

The amides **54** have been obtained by acylating the Schiff bases **53**,[166,167,172,173] while the urea derivatives **55** have been synthesised by condensing the bases **53** with phenyl isocyanate (Scheme 6).[149]

The reaction proceeds selectively with formation of the type A enamine structure only for X = CH$_2$, whilst in all the remaining cases equal amounts of the isomers A and B are obtained.

The condensation of the vinyl ethers of ethanolamine and propanolamine with paraformaldehyde leads to the products of the trimerisation of the azomethines **56** — the trivinyl ethers of 1,3,5-tris(2-hydroxyalkyl)hexahydrotriazine **57**.[162,174]

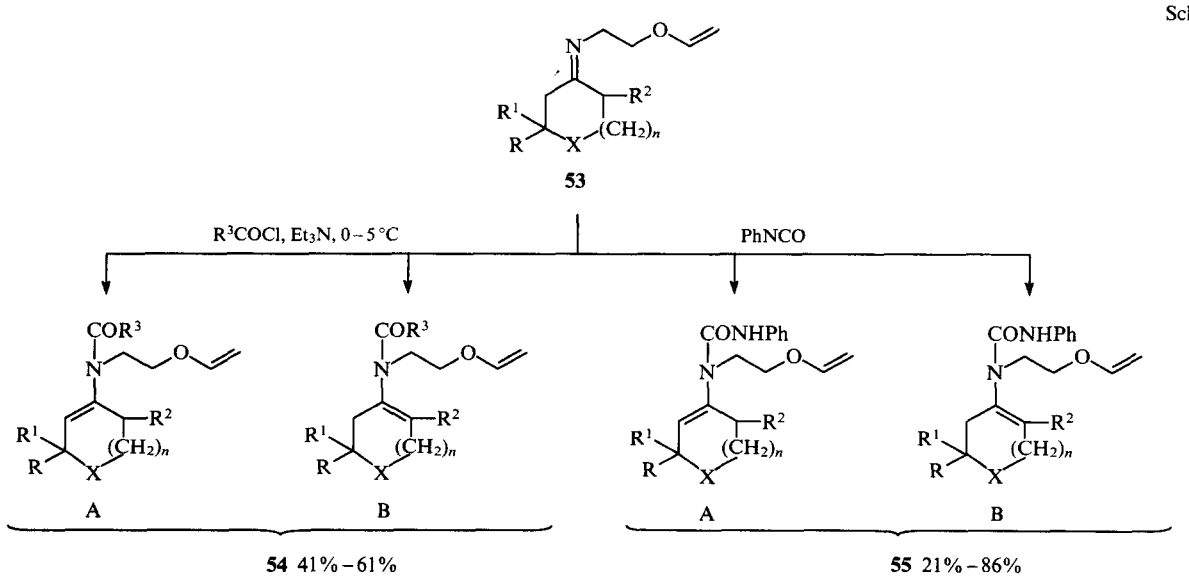


57 91%–94%

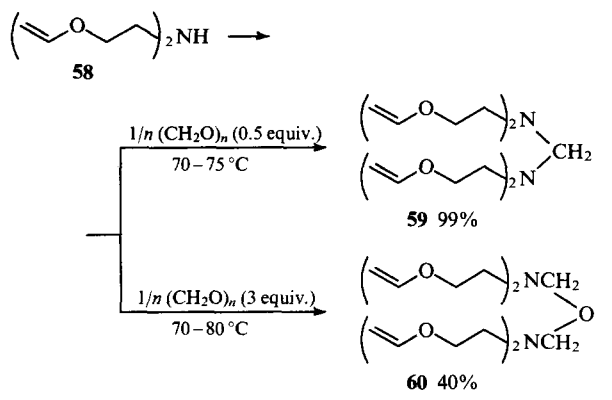
n = 2, 3.

N,N,N',N'-(2-Vinyloxyethyl)methylenediamine **59** has been obtained by the reaction of the divinyl ether of diethanolamine **58** with a stoichiometric amount of paraformaldehyde,[128,175] while in the presence of an excess of paraformaldehyde the product was the tetravinyl ether **60**.[102]

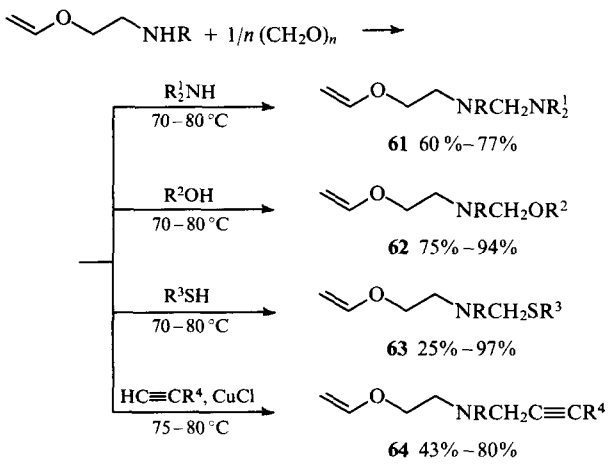
Scheme 6



n = 0, 1; R, R^1, R^2 = H, Me; R^3 = Me, Et, Pr, Ph; X = O, NMe, CH$_2$.



The vinyl ethers of aminoalcohols with a secondary amino-group and paraformaldehyde have been used for the amino-methylation of amines,[102] alcohols,[102,128] thioalcohols,[102] and ethynes[38,121,176-178] in the synthesis of the vinyl ethers of *N,N*-disubstituted aminoethanols **61**–**64**.



R = $CH_2CH_2OCH{=}CH_2$, CH_2CH_2COOEt, CH_2CH_2COOBu, $CH_2CHMeCOOMe$; R^1 = Et, $CH_2CH{=}CH_2$;

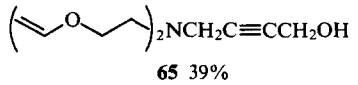
R^1_2 = $-CH_2CH_2OCH_2CH_2-$;

R^2 = Bu, $CH_2CH{=}CH_2$, $CH_2C{\equiv}CH$, $CMe_2C{\equiv}CCH{=}CH_2$, $CH_2CH_2OCH{=}CH_2$; R^3 = Bu, $CH_2CH{=}CH_2$, Ph;

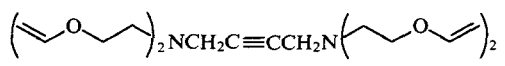
R^4 = H, Ph, $C{\equiv}CCH_2OH$, $C{\equiv}CCMe_2OH$

In the absence of catalysts, ethynyl alcohols are amino-methylated only at the hydroxy-group,[102] but in the presence of copper monochloride the aminomethylation takes place exclu-sively at the ethynyl group.[177]

The aminomethylation of ethyne by paraformaldehyde and the amine **58** gives rise to the formation of the aminoalcohol **65** and the diaminobutyne **66** together with propargylamine **64** (yield 18%).[177]

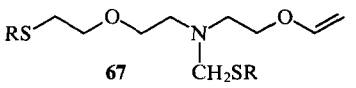


65 39%



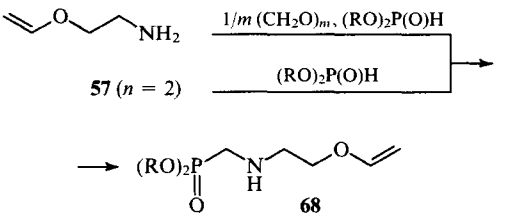
66 24%

The aminomethylation of thioalcohols is complicated by the side reaction involving the addition of the thioalcohols to the vinyl-oxy-group, as a result of which the sulfides **67** are obtained in yields up to 20% from the amine **58**, in addition to the sulfides **63**.[102]



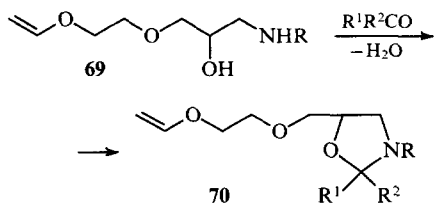
R = Bu, $CH_2CH{=}CH_2$.

When the vinyl ether of monoethanolamine and para-formaldehyde are used for the aminomethylation of dialkyl phosphites, the yields of the phosphonates **68** is significantly reduced. These compounds are obtained in satisfactory yields by the interaction of dialkyl phosphites with the triazine **57** (n = 2).[179]



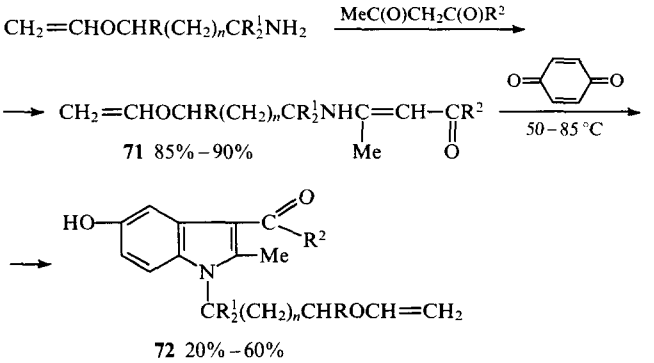
R = Et (43%), R = Bu (36%).

The vinyl ethers **69**, containing a hydroxy-group, condense with carbonyl compounds, affording the oxazolidines **70** in yields up to 91%.[180]



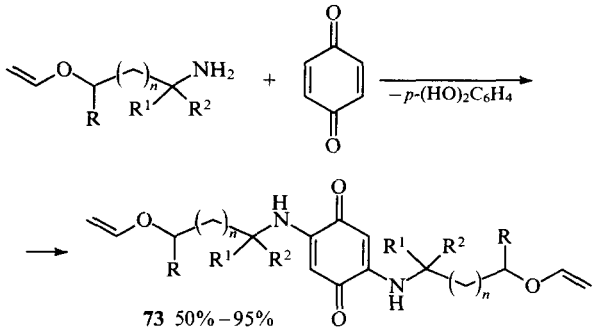
R, R^1, R^2 = H, Me, Et, Pr, Bu; $R^1 + R^2 = -(CH_2)_5-$.

Dicarbonyl compounds such as acetylacetone and aceto-acetic ester condense with VE AA, forming the enamines **71**,[149,167,181-183] the subsequent reaction of which with 1,4-benzoquinone leads to the indoles **72**.[182,183]



R, R^1 = H, Me, Et; R^2 = Me, OEt; n = 0–2.

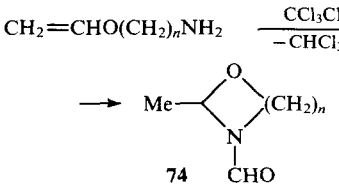
The interaction of 1,4-benzoquinone with VE AA, like that with primary amines,[184] involves an oxidation–reduction process, which results in the formation of the diaminobenzo-quinones **73**.[185,186]



73 50%–95%

R = R¹ = R² = H, Me, Et; *n* = 0–2.

The reaction of chloral hydrate with aliphatic amines is known to be accompanied by the formylation of the latter.[187] In the case of VE AA, not only their formylation but also their cyclisation to the 1,3-oxazacycloalkanes **74** take place.[188]

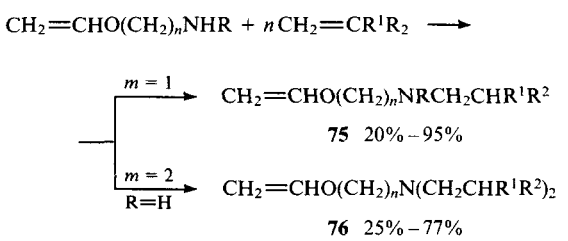


74

n = 2 (69%), *n* = 3 (56%).

5. Addition to carbon – carbon multiple bonds

Like the usual aliphatic amines, the vinyl ethers of aminoalcohols add to the activated C=C and C≡C bonds. For example, their addition to acrylonitrile,[189] acrylamide,[190] and the esters of acrylic[19,117,127] and methacrylic[127,191] acids has been described. Depending on the reactant ratio, the vinyl ethers with a primary amino-group can give rise to both the monoadducts **75** and the diadducts **76**.[117,127]



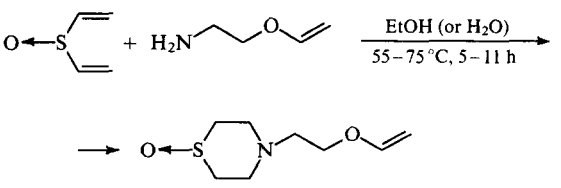
75 20%–95%

76 25%–77%

n = 2, 3; R = H, Me, $CH_2CH_2OCH{=}CH_2$; R^1 = H, Me;

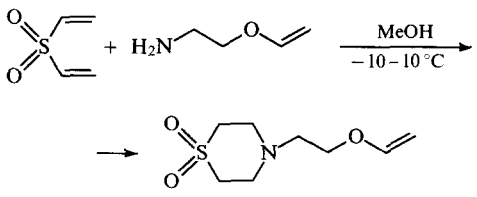
R^2 = CN, $CONH_2$, COOMe, COOEt, COOBu.

At a temperature above 50 °C, divinyl sulfoxide readily combines with the vinyl ether of monoethanolamine, affording 4-(2-vinyloxyethyl)-1,4-perhydrothiazine 1-oxide **77**.[114,115,192,193]



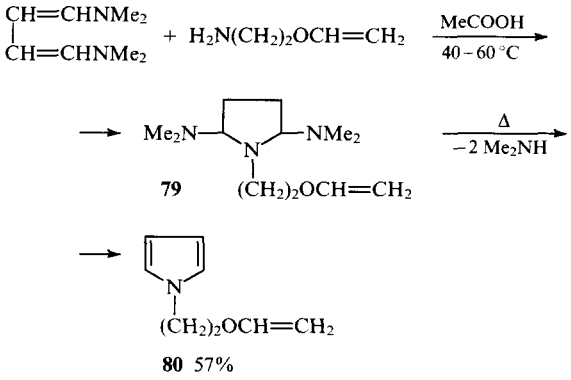
77 75%–85%

The reaction with divinyl sulfone takes place even on cooling, whereupon the sulfone **78** is formed.[194]



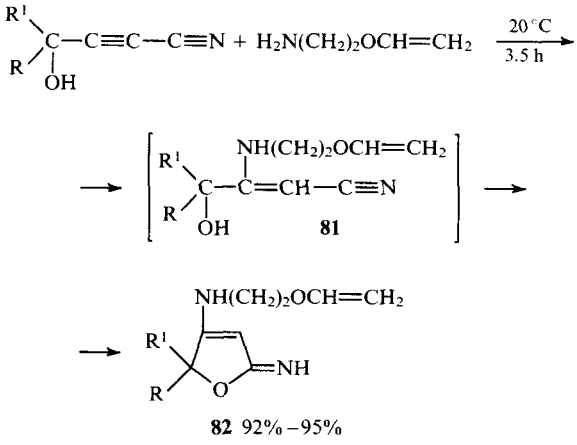
78 82%

The interaction of the vinyl ether of monoethanolamine with 1,4-bis(dimethylamino)buta-1,3-diene is exothermic in the presence of catalytic amounts of acetic acid. The pyrrolidine **79** formed is converted into 1-(2-vinyloxyethyl)pyrrole **80** during distillation.[195]



80 57%

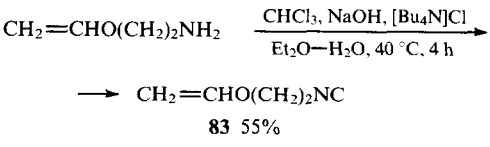
When the vinyl ether of monoethanolamine is added to the triple bonds of tertiary cyanoethynyl alcohols, the intermediate unstable nitriles **81** are formed initially and then cyclise to the furan derivatives **82**.[196]



82 92%–95%

R = R¹ = Me; R + R¹ = –$(CH_2)_4$–.

Under the conditions of phase transfer catalysis by tetrabutylammonium chloride, the interaction of the vinyl ether of monoethanolamine and the dichlorocarbene generated from chloroform results in the formation of 2-vinyloxyethyl isocyanide **83**.[197]

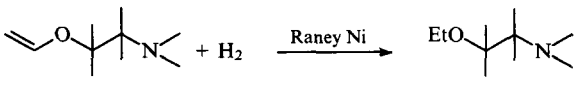


83 55%

6. Reactions involving addition to the vinyl group

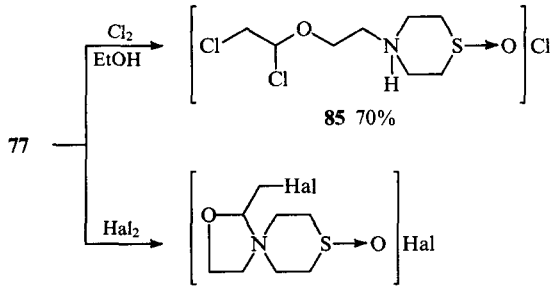
One of the reactions involving only the vinyl group is the hydrogenation of VE AA. The reaction is carried out on Raney nickel at temperatures in the range 20–150 °C and hydrogen pressures from atmospheric to 5 MPa. The yields of the ethyl ethers of aminoalcohols **84** are 65%–100%.[20,21,26,44,162,191,194,198–200]

The study of the hydrogenation of the vinyl ether of monoethanolamine on Raney nickel showed that the reaction is of zero order with respect to the vinyl ether and that its rate diminishes in the series of solvents ethanol > 1:1 ethanol–water > 1:1 dioxane–water > water.[199]



84

When chlorine adds to the vinyl ether **77** in ethanol, the hydrochloride of the dichloroether **85** is formed, whereas in aprotic solvents the product is the spiro-cyclic salt **86**. Regardless of the type of solvent, the interaction of iodine with compound **44** leads to the salt **86**.[114,201]

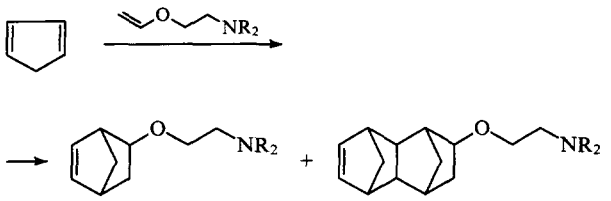


85 70%

86 95%–98%

Hal = Cl, I.

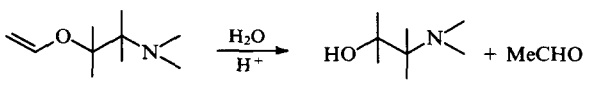
When the vinyl ethers of ethanolamines are used as dienophiles in the reaction with cyclopentadiene, the mono- and di-adducts **87** and **88** are formed in low yields.[202]



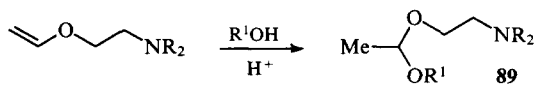
87 10%–17% **88** 6%–28%

R = H, Me, Et.

In acid aqueous solutions, VE AA are quantitatively hydrolysed to the aminoalcohols and acetaldehyde, but detailed studies of the hydrolysis have not been carried out. In the main, this reaction has been used to demonstrate the structure of the vinyl ethers.[18,20,21,26,44,99,191]



The vinyl ethers of aminoalcohols, which are stable in the presence of protic acids, are capable of combining with alcohols with formation of the acetals **89** when the reaction is catalysed by these acids.[20,21,24,203]



89

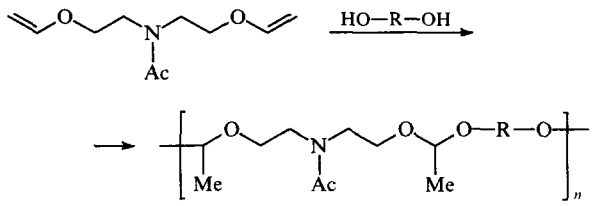
R = Et, R^1 = Bu (13%); R = Me, R^1 = $CH_2CH_2NMe_2$ (5%),

R = Et, R^1 = $CH_2CH_2NEt_2$ (6%); R = Ph,

R^1 = CH_2CH_2NHPh (62%); R = H, R^1 = $(AlkO)_2P(O)CH_2$ (70–82%).

Alk = Et, Pr^i, Bu.

When glycols are used as the alcohols, the reaction affords the oligoacetals **90**.[204]

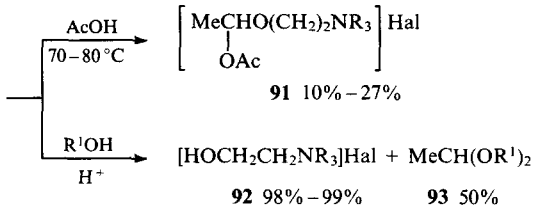


90 98%–99%

n = 4–7; R = $(CH_2)_2$, $(CH_2)_2O(CH_2)_2$, $(CH_2)_2O(CH_2)_2O(CH_2)_2$.

Quaternary vinyloxyethylammonium salts give rise to the adducts **91** with acetic acid, but are cleaved by alcohols when the reaction is catalysed by hydrochloric or sulfuric acids to the aminoalcohol salts **92** and the acetals **93**.[116]

$[CH_2{=}CHO(CH_2)_2NR_3]Hal$ ⟶



91 10%–27%

92 98%–99% **93** 50%

R = Me, Et; R^1 = Me, Et, Bu; Hal = Br, I.

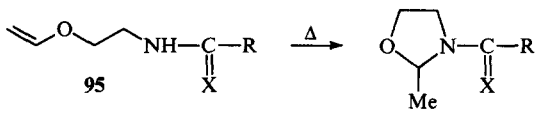
The addition of thioalcohols to the vinyloxy-group in VE AA proceeds, as in the case of alkyl vinyl ethers,[205] contrary to the Markovnikov rule with formation of the sulfides **94**.[67,102,124,141]

$CH_2{=}CHO(CH_2)_2NH_2 + EtSH \xrightarrow{100\,^\circ C,\ 6\ h}$

⟶ $EtS(CH_2)_2O(CH_2)_2NH_2$

94 20%–32%

Apart from the acid-catalysed cyclisation of vinyloxyalkylamines and vinyloxyalkylamides discussed above, it has been frequently noted that the cyclisation of certain amides **95** to the oxazolidines **96** can take place in the absence of acid catalysts. Thermal cyclisation has been observed at a temperature higher by 80–120 °C than in the acid-catalysed process.[95,96,104,105,137,138,156,206,207]

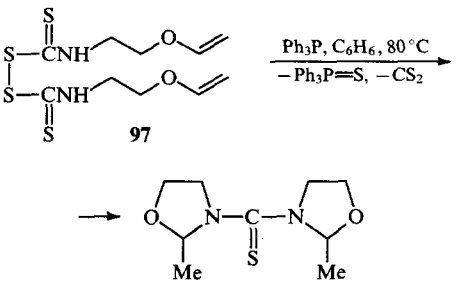


95 **96** 70%–100%

X = S, R = SBu, SCH_2Ph, $O(CF_2)_{6-10}H$;

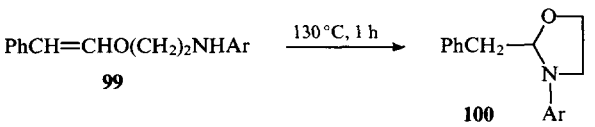
X = O, R = $OCH_2CH(OH)CH_2Cl$.

The unusual, not acid-catalysed, cyclisation of thiuram disulfide **97** to the thione **98** takes place when compound **97** interacts with triphenylphosphine.[208]



97 **98** 39%

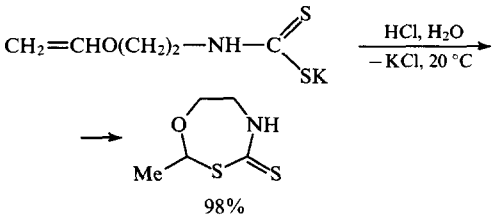
It has been shown recently[209] that the interaction of an aromatic substituent in the 2-position in the vinyloxy-group imparts to the ethers **99** the capacity for cyclisation to the oxazolidines **100** on treatment with bases. The thermal cyclisation of compound **99** does not occur.[65]



99 **100**

Ar = Ph (87%), 4-MeC_6H_4 (91%).

In the case of *N*-(2-vinyloxyethyl)dithiocarbamic acid, formed in situ from an aqueous solution of potassium carbamate and hydrochloric acid, the cyclisation takes place at the more acid SH group and not the amide group.[210]



98%

7. Polymerisation

In contrast to alkyl vinyl ethers for which cationic polymerisation is the main polymerisation reaction,[205] the vinyl ethers of aminoalcohols polymerise as a rule via a radical mechanism. This is associated with the deactivation of the cationic catalyst by the reaction forming a complex with the amino-group. Rare examples of the successful cationic polymerisation were examined above in the discussion of the reactions of vinyl ethers with acids.

2,2'-Azobisisobutyronitrile[19,21,26,211–225] or other azo-compounds[42,108,124,125] are usually employed to initiate the radical polymerisation. In the case of homopolymerisation, the reaction is carried out at 60–80 °C with 2%–5% of the initiator for 20–100 h. The yield of the polymers, which are viscous liquids with a low molecular mass (1000–2000), is usually low and ranges from 5% to 20%. Solid polymers with a three-dimensional structure are obtained under analogous conditions from certain divinyl ethers of diethanolamines and the trivinyl ether of triethanolamine in 40%–70% yields.[19,26,133,211,213]

The attempts to initiate the homopolymerisation of the vinyl ethers of ethanolamines by benzoyl peroxide were unsuccessful.[19,108,219] On the other hand, this initiator induces the polymerisation of quaternary vinyloxyalkylammonium salts.[83]

There are data on the initiation of the polymerisation of the vinyl ether **3** by γ-radiation.[226–229] It has been noted that in this case the degree of conversion of compound **3** into water-soluble polymers with quantitative retention of the amino-groups does not exceed 30%. For higher degrees of conversion of compound **3**, water-insoluble products are formed.

The use of elemental sulfur as the initiator of the polymerisation of the ether **3** has been described.[224,230] The polymer formed under these conditions contains up to 4.4% of sulfur and has a molecular mass of about 1000.

In order to investigate the reactivities of VE AA, they were copolymerised with other vinyl monomers, for example with methyl methacrylate,[125,191,212–214,219,231,232] acrylamide,[225,233,234] hexamethylenedimethacrylamide,[223] acrylonitrile,[42,225,231,232] divinylbenzene,[42] styrene,[150,225,232] vinyl chloride[150,153,231] *N*-vinylpyrrolidinone,[215,216,221,227,233–235] 4-vinylpyridine and 2-methyl-5-vinylpyridine,[216,235] 1-vinyl-4,5,6,7-tetrahydroindole,[236] the glycidyl vinyl diether of ethylene glycol,[217,218] the monovinyl ether of ethylene glycol,[154,237] and other vinyl ethers.[42,150,225,232,234,238]

The presence of the highly reactive amino-groups in the VE AA homopolymers makes it possible to achieve readily polymer-analogue reactions and to obtain in this way graft copolymers which are difficult to obtain by other procedures. For this purpose, the homopolymers were alkylated by alkyl halides and alkyl sulfates,[225,239–244] acylated by acid halides,[245] hydroxyalkylated by oxiranes,[243] and cyanoethylated by acrylonitrile.[246,247] The homopolymers were modified by condensing them with formaldehyde and acetylacetone,[97,243,248,249] by making them undergo the amide exchange reaction with urea,[250,251] and by their addition to isocyanates.[42,245]

IV. Practical applications

Although it is at present still impossible to say that the VE AA are employed as widely as, for example, vinyl ethers and esters, nevertheless the available literature data indicate considerable prospects for their use in industry, agriculture, and medicine.

In the study of their physiological activity, it was established that the vinyl ethers **16** (X = O) and the quaternary salts **19** exhibit hypotensive and spasmolytic activities.[75,85] Compound **77** and its salts may be used to correct the haemostasis in antithrombic therapy.[114,115,193] 2-Aryl-1-methyl-*N*-(2-vinyloxyethyl)-ethylamines reduce the appetite and are recommended for the treatment of obesity.[168,169] *N*,*N*-Bis(2-vinyloxyethyl)-*S*-(acylvinyl)dithiocarbamate and its salts possess a tuberculostatic activity.[252]

Effective fungicides,[42,119,150,152,238] insecticides[42,119,130,142,150,232] acaricides,[143,152] bactericides,[152] and bacteriostatic agents[94,152] have been found among VE AA derivatives.

The technical applications of VE AA are frequently associated with the solution of ecological problems. Thus they are employed for the detoxication of industrial waste by the elimination of heavy metals[163] and cyanides,[174,253] for the flotation purification of water by the elimination of organic suspensions (silt,[190] lignin[101,254]), and also for combating ore dust.[126] The employment of these compounds for the enrichment of muscovite[255,256] and polymetallic ores[146,257] not only increases efficiency but also makes it possible to reduce the amount of highly toxic reagents employed in these processes.

VE AA are used as intermediates in the synthesis of substances with analgesic, psychotropic,[258,259] and radio-protecting[141] properties. They are also employed to obtain corrosion

inhibitors,[42,139,152,154] plasticisers,[42,97,139,154] photostabilisers for plastics,[154] antioxidants for lubricating oils,[42,139] as fire-proofing reagents,[139] and as reagents imparting hydrophobic properties to materials of plant and animal origin.[97,231]

The polymers and copolymers obtained from VE AA are used as anion-exchange resins,[42,125,211] water-soluble complex-forming agents,[233,260] sorbents for transition and polyvalent metals,[42,223,233–235,243,248,261] flotation agents for the enrichment of polymetallic ores,[237,247,249,251,262,263] reagents for the removal of aldehydes, epoxides, and isocyanates,[42] as well as organic and mineral suspensions[239–243,246,250,264,265] from water, hardening agents for epoxide resins,[222,230] self-hardening epoxide resins,[217,218] adhesives,[109,130,150,217,218,238] plasticising[97,109,231,245] and antistatic[42,225] additives to plastics, coatings, and films,[42,97,125,150,152] auxiliary materials in the textile and cellulose-paper industries,[94,97,117,130,134,150,153,154,244,245] lubricating and hydraulic liquids or additives to them,[42,124] and fungicides and bactericides.[220,225]

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