SYNTHESIS OF HETEROCYCLES BY MEANS OF INTRAMOLECULAR RADICAL-ADDITION REACTIONS (REVIEW)*

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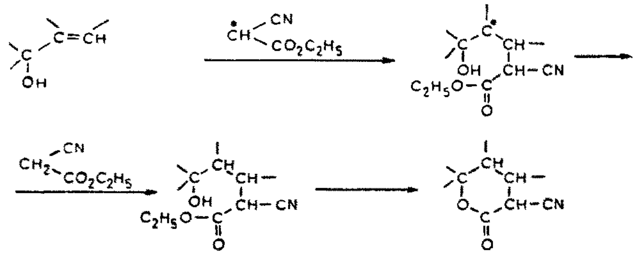
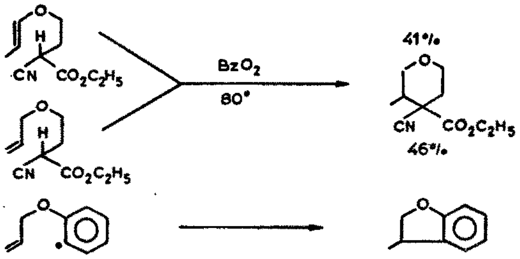
Methods for the synthesis of heterocyclic compounds based on intramolecular reactions with the formation of free radicals with an unpaired electron on the heteroatom as intermediate particles – photochemical cyclization of unsaturated nitrites, mercaptans, and sulfides and the photochemical and catalytic cyclization of unsaturated N-chloroamines – are examined.

The free-radical reactions that are most frequently used in the synthesis of organic compounds are usually of the following three types: replacement of a hydrogen atom, addition to double (or, less frequently, triple) bonds, and substitution reactions in the aromatic series.

However, up until 1964 only a very few methods for the synthesis of heterocyclic systems with the participation of free radicals were known, and this was the reason for our interest in this problem. First, it seemed possible to use the above-indicated reactions, for example, intermolecular radical-addition reactions, but to functional derivatives of olefins rather than to olefins themselves. There are many possibilities in this field, but their realization is limited by the inadequate amount of study of the behavior of such compounds with respect to free radicals. As an example, one may cite the radical addition of ethyl cyanoacetate to allyl alochols, which has proved to be a convenient method for the synthesis of δ-cyanolactones (in 30-80% yields) [1]:



A second possible direction was the use of intramolecular radical-addition reactions as applied to systems containing heteroatoms in the chain. Some oxygen-containing heterocycles have been obtained by this method [2, 3]



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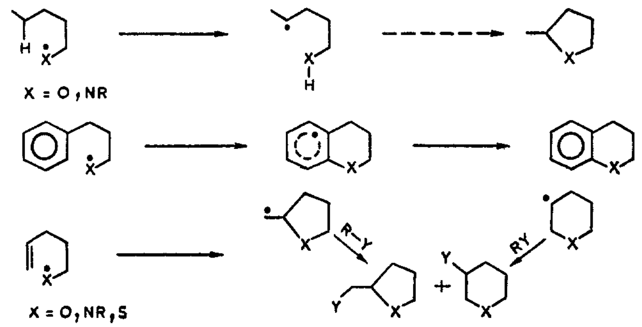
* Paper presented at the conference on the chemistry of heterocyclic compounds in La Grande Motte, France, May, 1973.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 579-593, May, 1975.

Finally, the investigation of intramolecular radical addition in which an unpaired electron is located on the heteroatom in the intermediate radicals might have been a third direction. The present review is devoted primarily to studies in this area performed in the author's laboratory and does not claim to give a complete account of the bibliographic material.

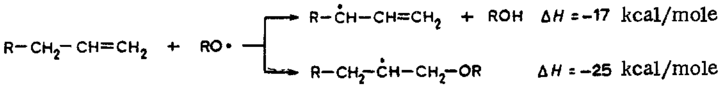


Of the three types of processes presented in the preceding scheme, the first – replacement of a hydrogen atom in the aliphatic series – was well known even before our studies [the Barton reaction (X=NO) and the Hofmann–Löffler–Freytag reaction]. The other two types have either received little study or have not been studied at all. The second type will be examined briefly, whereas primary attention in the review will be directed to the third type, inasmuch as, in particular, it has proved to be possible to observe not only intramolecular reactions similar to intermolecular reactions but also several new radical addition and cleavage reactions.

ALKOXYL RADICALS

Intermolecular substitution in the aromatic series with participation of an $R\dot{O}$ radical is observed extremely rarely: it possibly occurs during anodic methoxylation, in which neither $MeO^{\bullet}$ nor MeOH apparently participate and in the well-known but special (for alkoxyl radicals) case of hydroxyl radicals [generated by the Fenton reagent (H_2O_2/Fe^{2+}) or $H_2O_2/h\nu$]. The possibility of methoxylation was shown by Taylor [4] only in a special case in which the yield of substitution product did not exceed 20%.

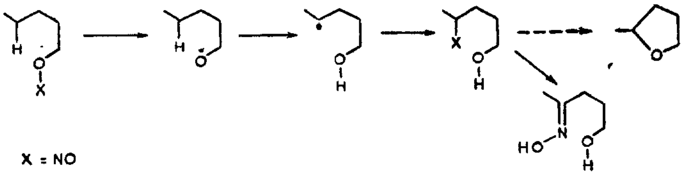
Processes involving β fragmentation and substitution of a hydrogen atom are the two most common reactions involving the participation of alkoxyl radicals. Addition to a double bond occurs only as an exception, and the mechanism of this reaction is not clear. At the same time, one should note that the ΔH value is more negative for addition than for substitution:



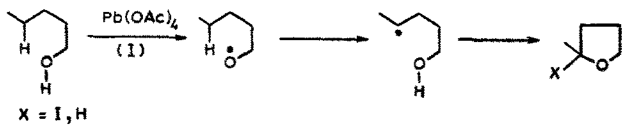
$$R{-}CH_2{-}CH{=}CH_2 + RO\cdot \begin{cases} \rightarrow R{-}\dot{C}H{-}CH{=}CH_2 + ROH & \Delta H = -17 \text{ kcal/mole} \\ \rightarrow R{-}CH_2{-}\dot{C}H{-}CH_2{-}OR & \Delta H = -25 \text{ kcal/mole} \end{cases}$$

Intramolecular Substitution Reactions in the Aliphatic Series

It has been found that intramolecular substitution reactions in the aliphatic series can be successfully used for the selective introduction of a functional grouping in the 5 position with respect to the oxygen atom by replacement of the hydrogen atom, which, according to classical concepts, should not be reactive. This is what is observed in the Barton reaction [5] (photolysis of nitrites, X=NO), which leads to the corresponding oximes, or in the photolysis of hypochlorites with the formation of chloro derivatives and subsequent cyclization to substituted tetrahydrofurans [6]:



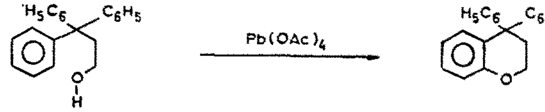
Treatment of alcohols with lead tetraacetate in the presence or absence of iodine gives tetrahydrofurans. Although the mechanism of this cyclization is as yet not completely clear, the homolytic character of the process, in which, however, the alkoxyl radical in free form does not participate [7, 8], seems extremely probable.



A disadvantage of all of these reactions is the fact that they can be used only for the synthesis of tetrahydrofuran derivatives.

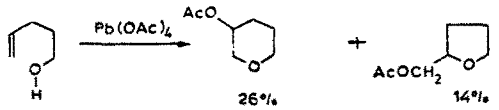
Intramolecular Substitution in the Aromatic Series

Little study has been devoted to the intramolecular substitution in the aromatic series with the participation of an alkoxyl radical. It has been shown [9] that this sort of process may be realized, but there is no complete confidence in its radical mechanism:

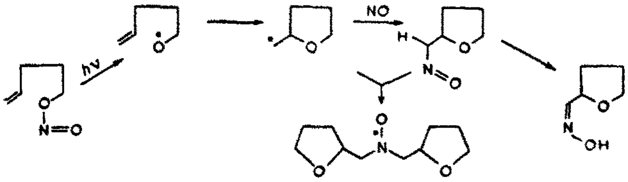


Intramolecular Addition to a Double Bond

It has been found that oxygen-containing heterocycles are formed in the reaction of lead tetraacetate with ethylenic alcohols, for example [10]

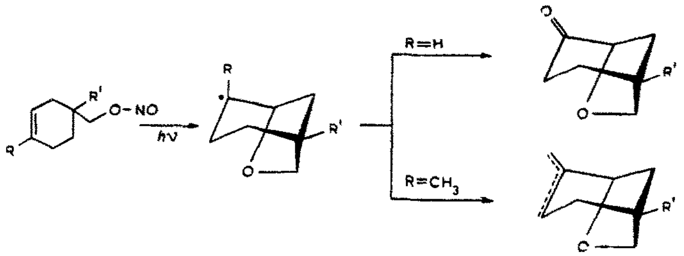


Although processes of this sort are not free-radical processes [10], it is precisely reactions of this sort that induced us to investigate the behavior of unsaturated alkoxyl radicals under conditions that exclude the possibility of an ambiguous interpretation of the results. We were able to show that nitrites of γ-ethylenic alcohols cyclize under the conditions of the Barton reaction to give tetrahydrofuryl-substituted oximes (in 50-60% yields) [11-16]:

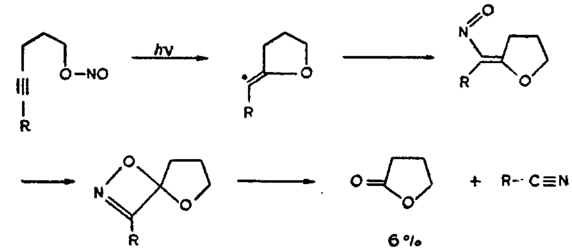


There is no doubt about the mechanism of this reaction (in any case, with respect to the part pertaining to the formation of an alkoxyl radical and its addition to the double bond). It is confirmed by the formation of a nitroxyl radical (by ESR) and chemical means [12].

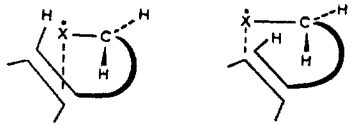
The cyclization of γ-ethylenic nitrites is an extremely general reaction. The presence of alkyl substituents attached to the carbinol carbon atom or to the double bond does not affect either the yield of the product of the reaction or its selectivity, which consists in the formation of only a five-membered ring. The reaction has also been used for the preparation of [3.2.1]-bicyclic systems (in ~30% yields) [17]:



However, we were unable to apply it to derivatives of acetylenic alcohols, probably because of cleavage of the intermediate unsaturated nitroso compounds [18]:



The selective formation of a five-membered ring rather than a six-membered ring is the rule for irreversible radical-addition products [19], although this selectivity does not always reach 100%. Two formally different attempts to give a qualitative explanation for this selectivity have become well known [20-22]. Our semiquantitative evaluation shows that the direction of cyclization may be associated with the magnitude of the van der Waals repulsion between the vinyl proton and the proton of the methylene group to which the atom having an unpaired electron is connected [23]:

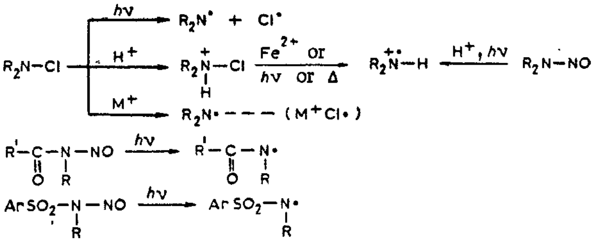


X	Formation of a five-membered ring	Formation of a six-membered ring
	Repulsion energy, kcal/mole	
O	0	15,4
C	0	12,4
R–N	0	12,2
S	0	1

The formation of a five-membered ring becomes increasingly more preferable as compared with the formation of a six-membered ring as the C–X bond becomes shorter. The greatest selectivity should be observed for alkoxyl radicals, whereas it will be extremely slight or even zero for RS• radicals: this was later confirmed experimentally.

AMINYL RADICALS

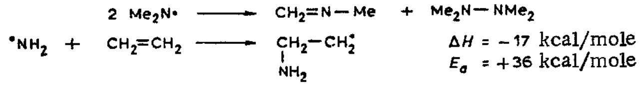
A number of reactive nitrogen-containing particles in which the nitrogen atom may have a valence from one to three or may be neutral or positively or negatively charged are known. Aminyl radicals of the $R_2N^\bullet$ type have reactivities that differ markedly as a function of the method used to generate them [24-27]:



$$R_2N{-}Cl \xrightarrow{h\nu} R_2N^\bullet + Cl^\bullet$$
$$R_2N{-}Cl \xrightarrow{H^+} R_2\overset{+}{N}(H){-}Cl \xrightarrow[h\nu\text{ or }\Delta]{Fe^{2+}\text{ or}} R_2\overset{+\bullet}{N}{-}H \xrightarrow{H^+,\,h\nu} R_2N{-}NO$$
$$R_2N{-}Cl \xrightarrow{M^+} R_2N^\bullet --- (M^+Cl^\bullet)$$
$$R'{-}C(=O){-}N(R){-}NO \xrightarrow{h\nu} R'{-}C(=O){-}N^\bullet(R)$$
$$ArSO_2{-}N(R){-}NO \xrightarrow{h\nu} ArSO_2{-}N^\bullet(R)$$

In addition, their reactivities also depend on the nature of R. All of these facts taken together open up broad prospects for the use of nitrogen-containing intermediates in organic synthesis.

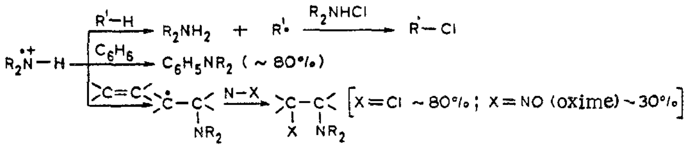
The reactivities of neutral aminyl radicals ($R_2N^\bullet$) are low, inasmuch as they primarily disproportionate to give imines and hydrazines [28], whereas the activation energy of addition to ethylene is extremely high, according to the results of the calculation in [29].



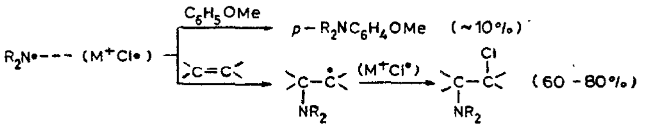
$$2\,Me_2N^\bullet \longrightarrow CH_2{=}N{-}Me + Me_2N{-}NMe_2$$
$$^\bullet NH_2 + CH_2{=}CH_2 \longrightarrow CH_2(NH_2){-}CH_2^\bullet \qquad \Delta H = -17\text{ kcal/mole},\quad E_a = +36\text{ kcal/mole}$$

On the other hand, neutral radicals of the $^\bullet NF_2$ or $RCO\dot{N}{-}R'$ type readily undergo addition reactions, although the interpretation of the mechanism of the process is ambiguous in this case [30, 31].

Protonated aminyl radicals are very reactive [32-35]. They can selectively replace a hydrogen atom in the aliphatic series [32] and undergo substitution reactions in the aromatic ring [33]. Addition rather than allylic substitution is observed more frequently in the presence of olefins. However, ionic chlorination is possible in the case of substituted olefins.

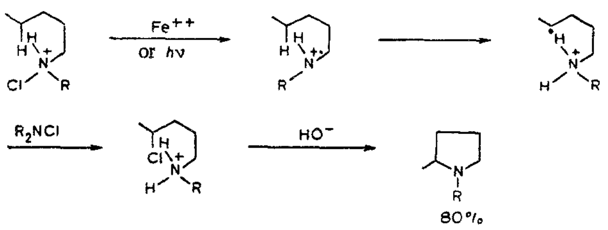


Substitution reactions proceed with greater difficulty in the case of complex aminyl radicals. Substitution in the aromatic series occurs only when electron-donor substituents are present, and electrophilic chlorination proves to be the major process in this case [36]. On the other hand, the addition of complex aminyl radicals to double bonds is a convenient method for the synthesis of β-chloroamines [37]:



Intramolecular Substitution Reactions

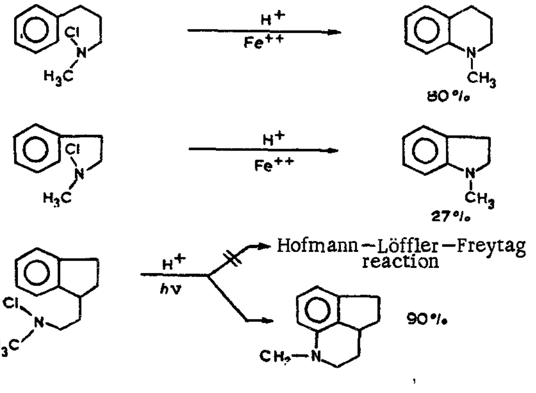
Intramolecular substitution reactions with an aminium radical have been investigated intensively in connection with their theoretical and practical interest [38] (the Hofmann–Löffler–Freytag reaction):



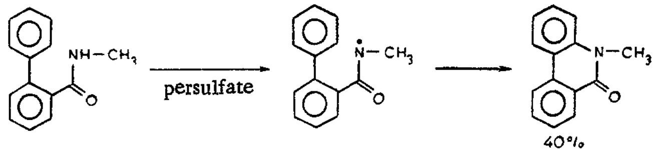
Because of its very high selectivity, this reaction cannot be extended to the preparation of heterocycles other than pyrrolidines. In contrast to amide or sulfamide radicals, neutral complex or aminyl radicals do not undergo the Hofmann–Löffler–Freytag reaction.

Cyclization of Aromatic Compounds

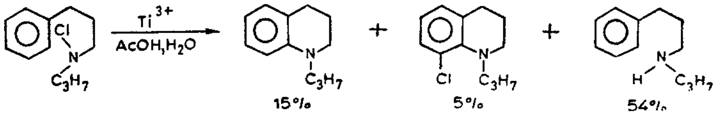
Little study has been devoted to the cyclization of aromatic compounds by means of aminyl radicals, although the published data make it possible to assume that some nitrogen heterocycles can be obtained via this route. Most of the studies were carried out with protonated aminyl radicals. In particular, tetrahydroquinolines were synthesized in excellent yields by this method [39]. When competition is possible, substitution in the aromatic ring is preferable to the Hofmann–Löffler–Freytag reaction [40]:



Recently investigated cyclization reactions involving the participation of amide and sulfamide radicals apparently proceed unambiguously [41–43]. Another mechanism (electron transfer) is also possible in the case of methyl-substituted compounds:

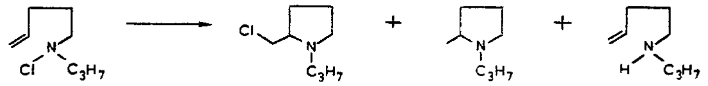


The behavior of aminyl radicals has not been studied in this respect, and complex radicals react more poorly than protonated radicals [44]:



Intramolecular Reactions of Ethylenic N-Chloroamines

The ease of intermolecular addition of N-chloroamines to double bonds induced us to consider the possibility of the synthesis of various nitrogen heterocycles by intramolecular reactions of ethylenic N-chloroamines [45–47]:



hν AcOH/H_2O (1:1)	70%	0%	0%
hν CH_3OH	24%	32%	9%
hν *i*-C_3H_7OH	6%	37%	18%
AcOH – H_2SO_4 (4*M*) (Fe^{++} or *hν*)	66%		
AcOH/H_2O (1:1), $TiCl_3$	81%		

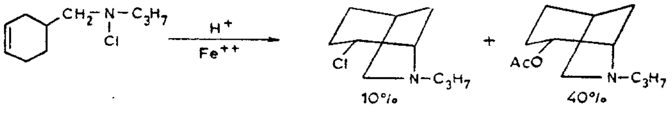
The photochemical cyclization of N-chloro-4-pentenylamine seems of special interest, inasmuch as it made it possible to demonstrate for the first time the possibility of intramolecular addition of a neutral aminyl radical [45]. It was shown that the detachment of a proton from the solvent becomes more important in a proton-donor solvent (in methanol or, to a greater degree, in isopropyl alcohol) than intramolecular addition.

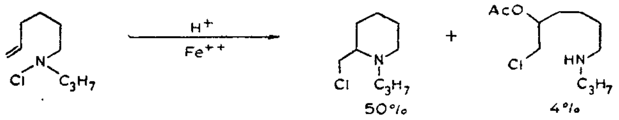
Reactions in acidic media require the observance of special precautionary measures, inasmuch as, for example, the presence of even traces of oxygen causes the mechanism of the process to become ionic (cyclic compounds are, nevertheless, obtained in this case also). In an experimental respect, intramolecular reactions are carried out most simply in the presence of a complexing agent [47].

It should be noted that intromolecular addition is preferable to the Hofmann–Löffler–Freytag reaction.

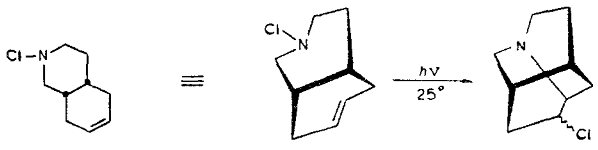
The high selectivity of all of these reactions, which lead to the formation of a five-membered pyrrolidine ring, makes them an interesting synthetic complement of the Hofmann–Löffler–Freytag reaction.

The range of application of the reaction is somewhat limited in acidic media in connection with the fact that electrophilic chlorination reactions occur to a significant degree in the case of olefins with substituted double bonds. Nevertheless, an intramolecular reaction is also observed under these conditions in a number of cyclohexenylmethyl- [48] and 5-hexenyl-substituted N-chloroamines [23] (however, the yields are higher when a complex radical is used):

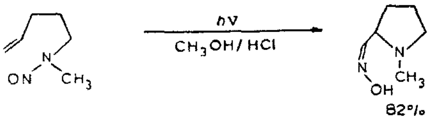




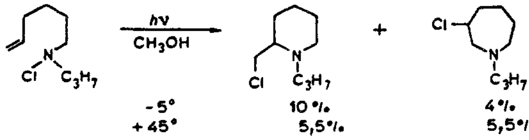
The preparative value of these reactions is particularly high in some cases. For example, azatwistane was obtained in 80% yield by this method [49]:



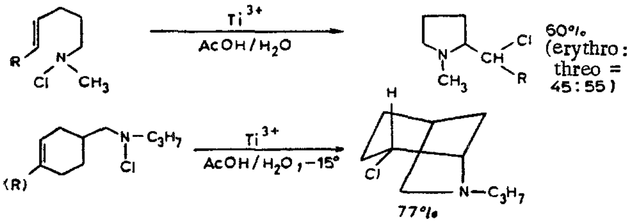
The photolysis of ethylenic nitrosamines in a methanol solution of hydrogen chloride leads to pyrrolidinyl-substituted oximes through a step involving the formation of an aminium radical [50, 51]:



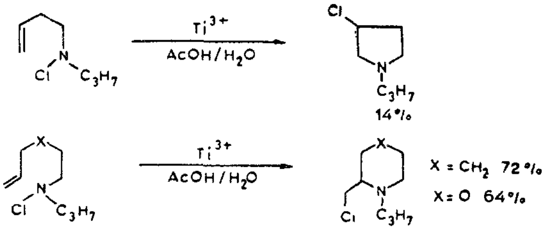
The results obtained when neutral aminyl radicals are used are usually poorer than in the case of complex radicals. However, even in these cases compounds that are difficult to prepare by other methods can sometimes be obtained [44]:



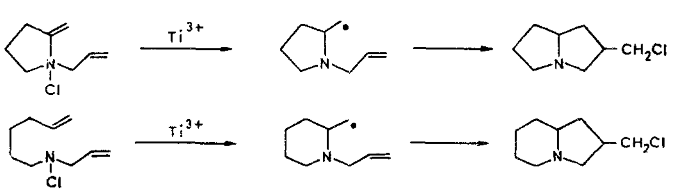
We have studied the behavior of complex radicals in greatest detail. In a number of pentenyl-substituted amines the presence of substituents at the end of the chain does not have a substantial effect on the yields [44]: Bicyclic systems are also formed in good yields [48], and the cyclization product presented in the scheme below is stereochemically individual:



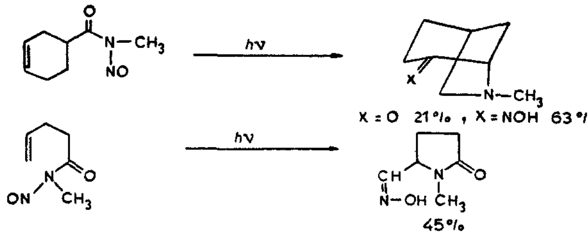
The reaction can also be extended to N-chloroaminobutenes [44]. Although the yields here are low, it should be noted that cyclization products are not formed at all in the case of analogous radicals that have an unpaired electron on the oxygen or carbon atoms. This reaction can also be extended to N-chloro-5-hexenylamines and their analogs, and six-membered heterocycles are obtained here in good yields [44]:



However, the results of cyclization of N-chlorodialkenylamines are of greatest interest in a preparative respect. Thus chloromethylpyrrolizidine was obtained as the only reaction product in 63% yield [44], and this reaction was used in the synthesis of indolizidines (in 50% yields) [52]:

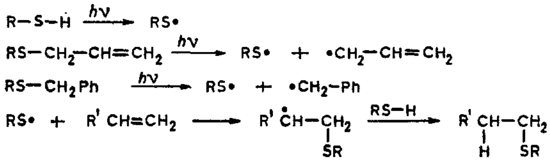


Several other radicals, for example, amide radicals, also undergo similar intramolecular addition reactions. The radical character of the reaction was confirmed by ESR spectroscopy [53, 54]. Unfortunately, ethylenic nitrosamides are difficult to obtain:



THIYL RADICALS

Photolysis of mercaptans is the most well-known method for the generation of thiyl radicals. We also used the photolysis of allyl or benzyl sulfides to obtain radicals of this type:



$$R\text{–}S\text{–}H \xrightarrow{h\nu} RS\bullet$$

$$RS\text{–}CH_2\text{–}CH{=}CH_2 \xrightarrow{h\nu} RS\bullet + \bullet CH_2\text{–}CH{=}CH_2$$

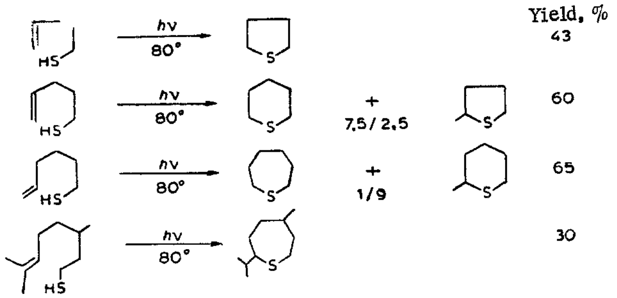
$$RS\text{–}CH_2Ph \xrightarrow{h\nu} RS\bullet + \bullet CH_2\text{–}Ph$$

$$RS\bullet + R'CH{=}CH_2 \longrightarrow R'\dot{C}H\text{–}\underset{SR}{CH_2} \xrightarrow{RS\text{–}H} R'\underset{H}{CH}\text{–}\underset{SR}{CH_2}$$

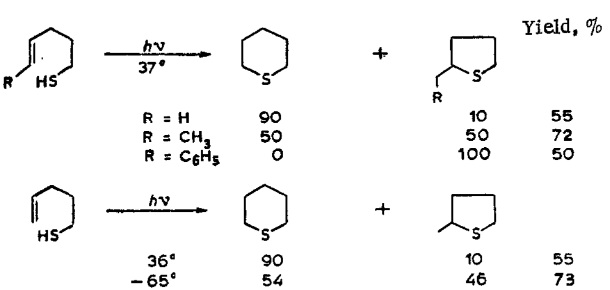
Up until recently the only known reaction of thiyl radicals was their intermolecular addition to a double bond. The reversibility of this process has been shown in various studies, including our studies, and the role of the reverse process is intensified as the temperature is raised.

In order to accomplish intramolecular reactions, we initially investigated the photolysis of ethylenic mercaptans, which are readily obtained from the corresponding halo derivatives through the isothiuronium salts. Even in our initial studies [55] we were able to show that intramolecular addition, which leads to sulfur heterocycles, is a general reaction, but, in contrast to what was observed in the case of alkoxyl and aminyl radicals, the reaction is nonselective and gives a mixture of two heterocycles in a ratio that depends both on the reaction conditions (temperature and reagent concentration) and on the structure of the mercaptan or sulfide (the length of the carbon chain and the nature of the substituents attached to the double bond). We have also demonstrated the radical character of the process: intramolecular addition of a thiyl radical to give a cyclic radical, which can be observed as the nitroxide by ESR spectroscopy after trapping with tert-C_4H_9NO.

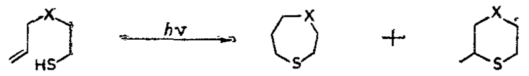
Some data characterizing the limits of applicability of the reaction are presented below [56]:



The effect of substituents and temperature on the ratio between the five- and six-membered rings is shown in the following scheme [56]:



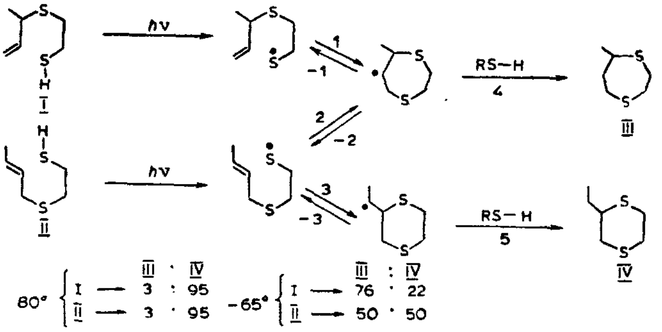
If there is a possibility of formation of six- and seven-membered rings, primarily the former is formed at 80°, and the presence of substituents at the end of the chain promotes this, whereas their presence in other positions favors the formation of a seven-membered ring [56]. In the general case, increasing the temperature promotes the formation of a six-membered ring, whereas an increase in the solution concentration promotes the formation of a seven-membered ring [56]:



				Yield, %
X = O	80°	15	85	44
	-65°	58	42	47
X = CH_2	80°	10	90	60
	-65°	78	22	62
X = S	80°	33	67	43
	20° 0.06 *M*	42	58	
	20° 1.44 *M*	67	33	
	-65°	88	12	45

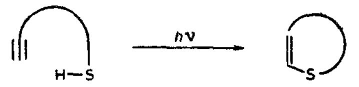
Thus, in principle, by changing the temperature and concentration one can direct the reaction to favor the formation of rings of either size.

The absence of selectivity and the change in the ratio between the reaction products as a function of the reaction conditions are explained by two reasons. First, because of the large C–S bond length, repulsion between the vinyl and methylene protons is weakened, and this leads to a decrease in the difference in the energies of the transition states leading to rings with n or n+1 links (see the repulsion energies given above). Second, these facts are associated with the reversibility of the reaction, which we have shown in one special example [57]:



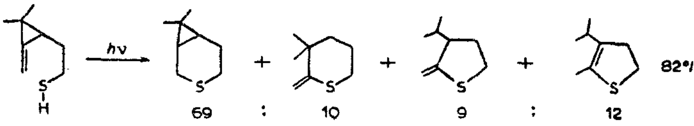
The role of the reverse reaction increases as the temperature rises. We note that the formation of dithiane IV from mercaptan I in general cannot be convincingly explained in any other way than as the result of free cyclization of the intermediate seven-membered radical. At high temperatures the reaction is completely reversible, and, in particular, reactions –2 and –3 are faster than reactions 4 and 5, and this leads, regardless of the starting mercaptan, to the same IV to III ratio (95 : 3). At low temperatures the rates of reactions –2 and –3 becomes lower than the rates of reactions 4 and 5, and, although recyclization is still observed at –65° (mercaptan I gives 22% of dithiane IV), it is seen that primarily dithiepan III is obtained in this case from I. In addition, primarily a seven-membered ring rather than a six-membered ring is formed from mercaptan II at low temperature because of kinetic control. Finally, there is still another possibility for a decrease in the rate of recyclization by creation of more favorable conditions for detachment of a proton (an increase in the solution concentration promotes the formation of a seven-membered ring).

The yields of cyclization products formed in the photolysis of acetylenic mercaptans are lower than the yields obtained in the photolysis of ethylenic derivatives [58]. This is due to the high reactivities of unsaturated heterocycles. In the case of monosubstituted acetylenes the reaction proceeds only at the terminal carbon atoms; when there is an alkyl group in this position, addition in both directions is possible:

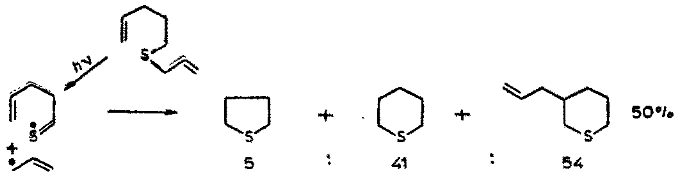


Ring size	5	6	7	8	9
Yield, %	–	48	38	23	8

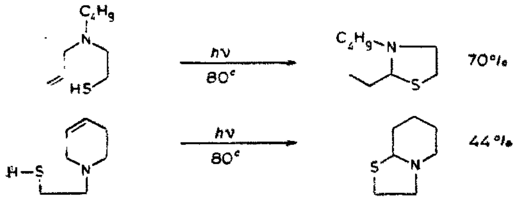
An attempt to extend this reaction to methylenecyclopropane derivatives seems of interest. An attempt of this sort led mainly to normal addition products and, partially, to products of rearrangement of the intermediate radicals [59]:



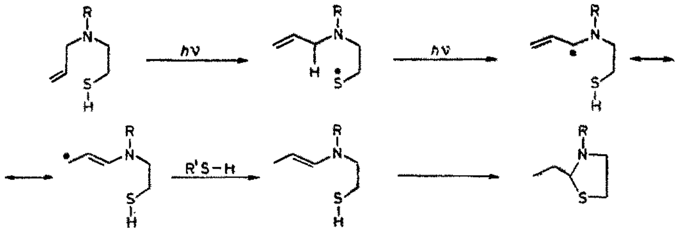
Recombination of cyclic and allyl or benzyl radicals was observed in the cyclization of allyl or benzyl alkenyl sulfides [60]:



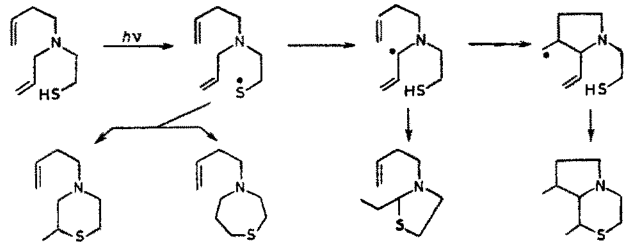
Assuming that the cyclization of N-(2-mercaptoethyl)-N-allylamines gives, as in the case of the other compounds that we investigated, six- or seven-membered rings, we unexpectedly obtained thiazolidines in this case [56, 61]. Six- or seven-membered systems are obtained in low yields only at higher temperatures:



The thiazolidines are not formed as a result of possible rearrangement of the intermediate heterocycles. The scheme for their formation is based on the assumption that when certain prerequisites are met, the thiyl radical more likely undergoes intramolecular substitution of the hydrogen atom rather than addition. These prerequisites are, first, that the intermediate radicals should have a structure analogous to the structure of the intermediate radical in the Barton radical; second, that the hydrogen atom undergoing replacement should be of the allyl type; and, third, that a nitrogen atom should be situated in the α position relative to this hydrogen atom. However, it is surprising that this reaction is not observed in the case of oxygen-containing analogs:



In order to verify this hypothesis, we carried out the same reactions with an amino thiol in which R = butenyl [62]:



	V		VI		VII		VIII	
36(hν)	57	:	8	:	33	:	2	35%
130° tert-Bu$_2$O$_2$	19	:	3	:	27	:	51	67%

The formation of VIII corresponds to the proposed scheme: it may be obtained as a result of selective addition of the carbon atom of the allyl radical to give the pyrrolidine. The latter, being simultaneously an unsaturated mercaptan, undergoes subsequent cyclization, especially at high temperatures, to give a six-membered ring. The fact that "normal" addition is observed primarily at low temperatures is in all likelihood associated with the reversibility of the addition of the RS• radical, the role of which increases as the temperature rises. An increase in the temperature also promotes the substitution reaction, which has a high activation energy. In conclusion, it should be pointed out that the study of free-radical reactions may lead to the detection of interesting methods for the synthesis of heterocyclic compounds. The already well-known intermolecular reactions can be used for this purpose. However, one must take into account the fact that drawing together of the radical and any other reactive center may bring about the occurrence of new processes that are presently unknown in the chemistry of intermolecular reactions.

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