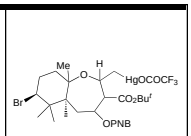
Preparation of seven and larger membered heterocycles by electrophilic heteroatom cyclization



CHEMICAL SOCIETY REVIEWS

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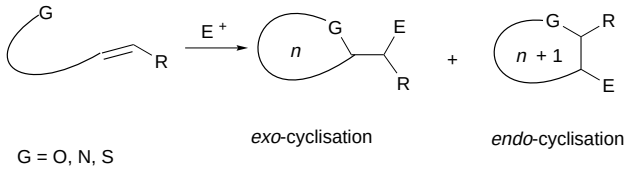
The preparation of seven and larger membered ring compounds from linear substrates is known to be a difficult process. We report results for the preparation of heterocycles with these ring sizes by electrophilic heteroatom cyclizations. Examination of the literature shows that the obtention of seven-membered compounds is possible in good yields by a proper choice of the electrophilic reagents, while for eight- and larger membered compounds these cyclisations are possible only if steric constraints are introduced into the chain.

1 Introduction

Since the discovery of the iodolactonization reaction of β,γ- and γ,δ-unsaturated carboxylic acids by Bougault,[1] electrophilic heteroatom cyclization has been the subject of much research.[2] However, if the formation of three to six membered ring heterocyclic compounds has been reported (Scheme 1), few examples could be found in the literature for larger rings, until recently. This absence of results was indeed the result of unsuccessful attempts.[3]



Scheme 1

The difficulty in preparing seven and medium ring compounds by cyclization methods has been known for some time.[4] In an interesting study involving the formation of lactones (ring sizes 3 to 23) from ω-bromoalkanoates, Illuminati and Mandolini[5] have illustrated this problem well (Fig. 1). A maximum rate of cyclization was observed for the formation of

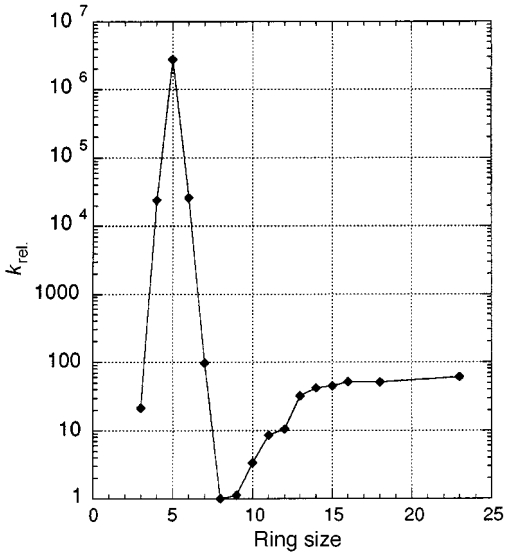


Figure 1

γ-butyrolactone and then the rate decreased dramatically for the 7-(by a factor of 10^4) and 8-membered ring lactones (by a factor of 10^6). A slow increase in the cyclization rate was then observed. From a synthetic point of view, these constant rate values mean that good yields should be expected for the formation of 4–6 membered ring lactones, while low to very low yields should be obtained in the other cases.

To circumvent this intrinsic factor, different solutions have been sought. The most obvious, *i.e.* the use of high-dilution conditions is not applicable in this case, due to the fact that the kinetics for electrophilic cyclization are second order. The solution to this problem must be found in the modification of the substrates and/or the electrophiles. Nucleophilic atoms which can be used in these electrophilic heteroatom cyclizations are

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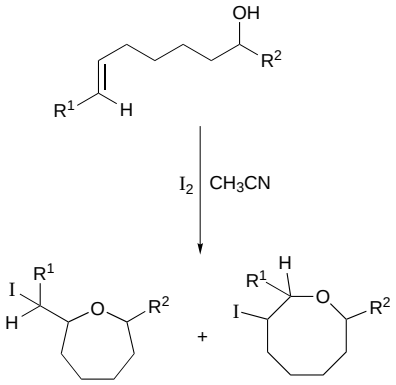
mainly O, N and S. No example with S is known for the formation of rings larger than six. In Table 1 we report the common names of medium ring heterocycles which are not familiar to the majority of organic chemists.

The mechanism of electrophilic cyclizations has not yet been completely elucidated. Formation of an onium ion or a concerted attack of the nucleophile on a π halogen double bond complex have been proposed.[6] It is probable that both mechanisms can exist depending on the nature of the electrophile.

2 Oxygen as nucleophile

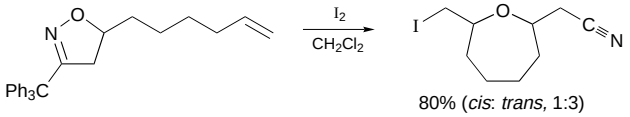
2.1 Formation of cyclic ethers by *exo*-mode cyclization

It has been reported that hept-6-enol derivatives react with iodine in acetonitrile to give oxepanes and oxocanes in low yields (15–30%).[7] In all cases the oxocanes (8-membered ethers) were the minor products (Scheme 2).



Scheme 2

These yields were subsequently improved by modifying the substrates and the electrophiles. It was reported that an isoxazoline, substituted in the three position by a trityl group, reacted with iodine in methylene chloride to give an oxepane in 80% yield.[8] (Scheme 3). The driving force of this reaction seems to be the formation of the thermodynamically favoured nitrile function. However, this strategy did not allow the preparation of the corresponding oxocane.

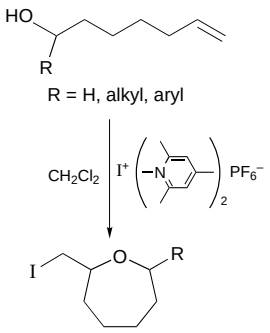


80% (*cis*: *trans*, 1:3)

Scheme 3

We found that instead of modifying the substrate, it was possible to modify the iodide reagent. Indeed, using bis(collidine)iodine(I) hexafluorophosphate in methylene chloride we observed the iodoetherification of hept-6-en-1-ols in good yields (Scheme 4).[9] The success observed in these cyclizations compared to the iodine reagent is due to the absence of a reactive counter anion. No diastereoselectivity was observed. In previous work, 1,4-dioxepane was obtained in only 12% yield using bis(collidine)iodine(I) perchlorate.[10]

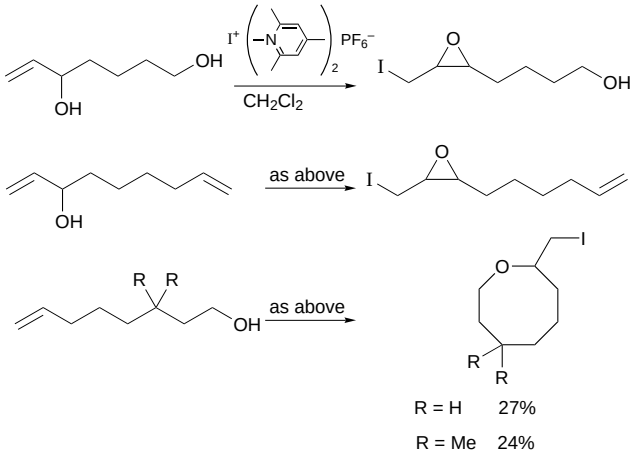
Different substrates were used to study the competition between 3-*exo*-/7-*exo* cyclization. Only the 3-*exo* cyclization



65–95% (*cis*: *trans*, 50:50)

Scheme 4

was observed which reflects the importance of the entropy factor in these cyclizations. With the same reagent, oxocanes were obtained in moderate yields. This last result illustrates well the difficulty of obtaining 8-membered ring compounds compared to 7-membered ring compounds.[9] (Scheme 5).



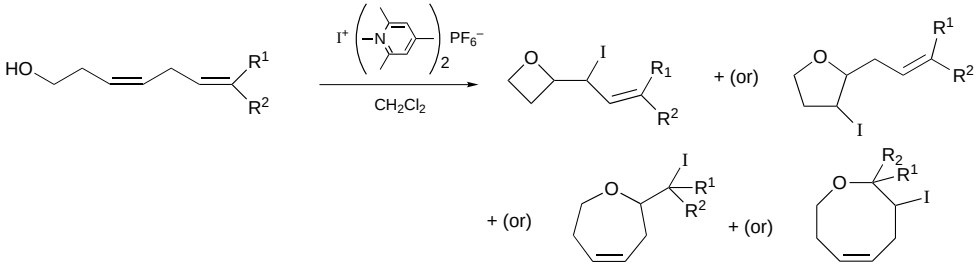
Scheme 5

We have also examined the preparation of oxepenes by iodoetherification, starting from 3,6-heptadien-1-ols. This kind of substrate is interesting since 4-*exo*, 5-*endo*, 7-*exo* and 8-*endo* cyclizations are in competition. Depending on the substitution at the terminal double bond all these modes of cyclization could be observed, albeit in low yields (24–44%) (Scheme 6). The unsubstitued substrate (R^1 = R^2 = H) led mainly to the oxepene (36% yield). Introduction of an *E*-methyl (R^1 = H; R^2 = Me) favoured the 5-*endo* cyclization (29% yield), while its *Z* isomer (R^1 = Me; R^2 = H) led mainly to the oxocene (18% yield). Introduction of two methyls (R^1 = R^2 = Me) had a negative effect and only the 5-*endo* and 4-*exo* cyclizations products could be detected in low yields (14 and 9% respectively). In fact, contrary to what was expected, substitution at the terminal double bond had a negative effect due to the increase of steric hindrance which disfavoured the formation of 7- or 8-membered rings. This phenomenon appears to be general for these ring sizes (*vide infra*).

The presence of a substituent in the 6-position allowed the exclusive formation of oxepenes in good yields. The corre-

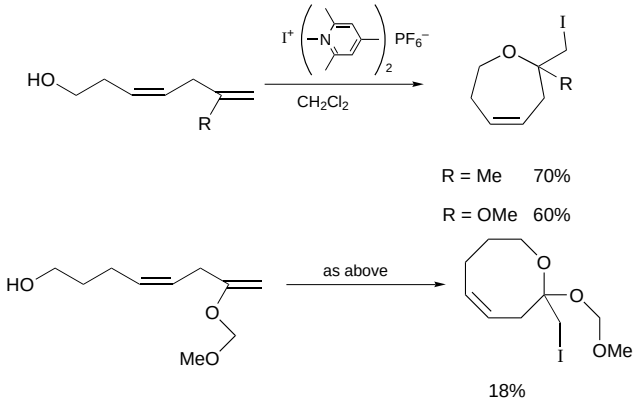
Table 1 Chemical names of medium ring heterocycles

Ring size	Ether	Lactone	Amine	Lactam
7	Oxepane	Oxepan-2-one	Azepane	Azepan-2-one
8	Oxocane	Oxocan-2-one	Azocane	Azocan-2-one
9	Oxonane	Oxonan-2-one	Azonane	Azonan-2-one
10	Oxecane	Oxecan-2-one	Azecane	Azecan-2-one
11	Oxacycloundecane	Oxacycloundecan-2-one	Azacycloundecane	Azacycloundecan-2-one



Scheme 6

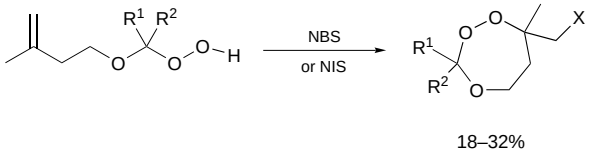
sponding oxocene was formed, again in low yield.[9] (Scheme 7).



Scheme 7

It has been reported that this cyclization could also be carried out with silanols, but apparently with lower yields than with alcohols. The presence of substituents on the carbon–carbon double bond allowed the competitive formation of *endo* cyclization products[11] (Scheme 8).

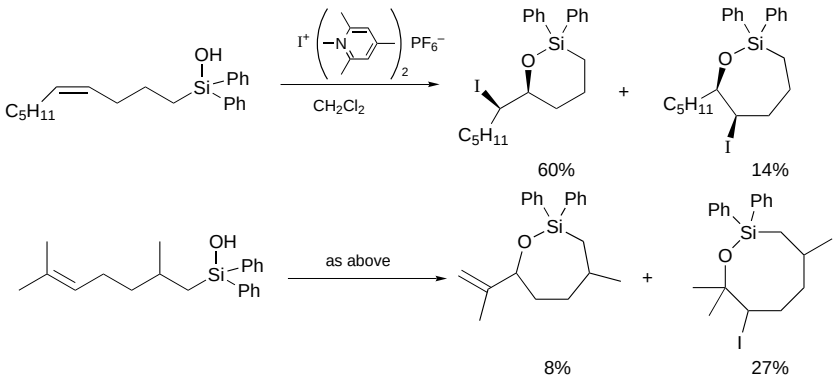
Other reagents were tested for the formation of oxepanes. Biomimetic cyclizations of different dienols were attempted for a short synthesis of aplysistatin. Low yields (25–30%) were observed using mercury(II) trifluoroacetate or tetrabromobenzoquinone as electrophiles.[12] The cyclization was improved using conformationally more rigid molecules (66–92% yields)[12a] (Scheme 9).



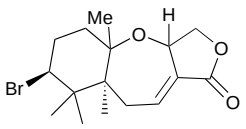
Scheme 10

While NBS or NIS are unable to induce the formation of oxepanes from hept-6-enols,[9] it was recently reported that 1,2,4-trioxepanes could be obtained in moderate yields by cyclization of the corresponding hydroperoxides. This partial success is probably due to the higher nucleophilicity of the terminal oxygen of the hydroperoxide compared with that of the alcohol (Scheme 10).[13]

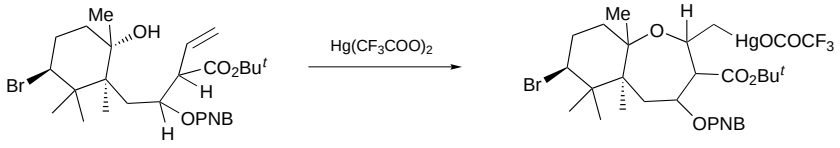
Phenylsulfenoetherification was reported to be a possible route for the formation of oxepanes, using phenylthiomorpholine in the presence of trifluoromethanesulfonic acid to generate the episulfonium ion (Scheme 11).[14] In this case also,



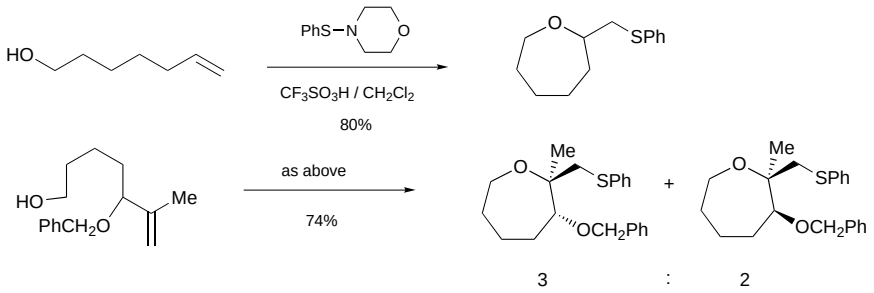
Scheme 8



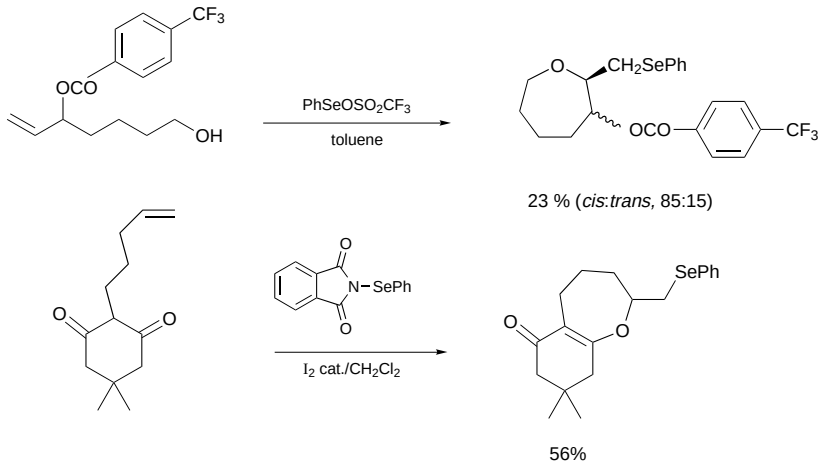
aplysistatin



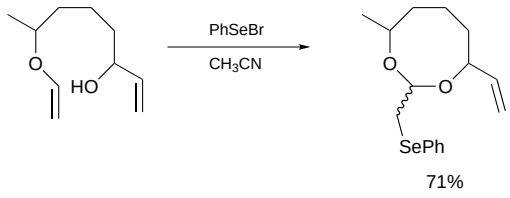
Scheme 9



Scheme 11



Scheme 12



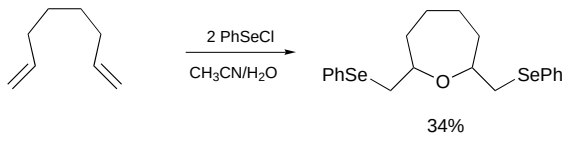
Scheme 13

the presence of the substituents on the terminal carbon of the double bond allowed, surprisingly, the competitive formation of oxocanes.

Phenylselenoetherification also appears to be an efficient method to prepare oxepanes, though few examples are available. Cyclization was observed in the reaction of unsaturated alcohols with $PhSeOSO_2CF_3$[15] or *N*-phenylselenophthalimide[16] (Scheme 12).

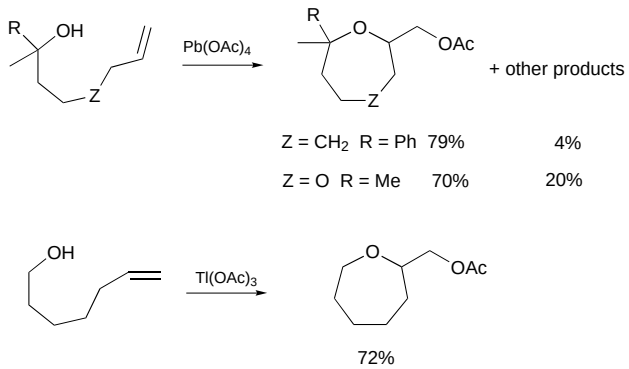
Phenylselenobromide was found to be efficient for the formation of 1,3-dioxocane.[17] The success of this cyclization seems due in part to the presence of an electronically enriched carbon–carbon double bond (Scheme 13). (Compare, however, with the example shown in Scheme 7). This is the best example reported to date concerning the preparation of an oxocane by electrophilic cyclization.

Phenylselenochloride was equally efficient for the cyclization of 1,7-octadiene in the presence of water[18] (Scheme 14).



Scheme 14

Treatment of hept-6-enols with lead tetraacetate was found to lead in some cases to oxepanes.[19] However, very often these electrophilic cyclizations were not specific and rearrangement compounds were isolated as side or main products. It appears that for this cyclization, thallium triacetate was more efficient,[20] since the oxepane was obtained as a unique product (Scheme 15). Oxocanes could not be obtained with these conditions. While with thallium triacetate no 6-*exo*-/7-*endo* competition



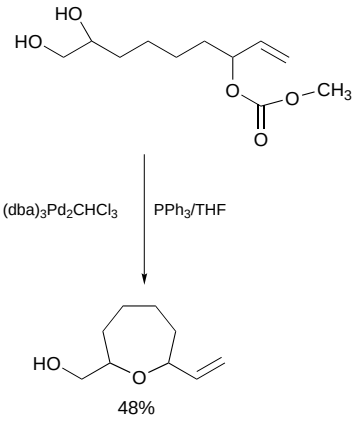
Scheme 15

was observed during the cyclization, with benzene tellurenyl acetate (PhTeOAc) such a competition did take place.[21]

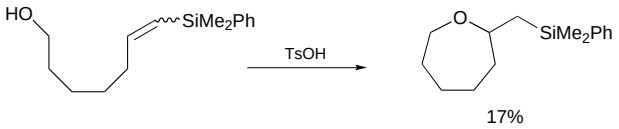
Palladium was also found to be useful for the cyclization of heptenols and led to the formation of 1,6-disubstitued oxepanes (Scheme 16).[22]

Alkenols are in general inert in the presence of TsOH. It was reported that if a silicon atom was fixed on the carbon–carbon double bond, then the cyclization could take place and an oxepane was isolated in low yield.[23] Such a reaction could probably be improved by using more efficient electrophiles (Scheme 17).

Electrophilic cyclizations are not limited to double bonds, and examples starting with acetylenic and allenic derivatives which are generally more reactive[24] have been reported for the formation of 5- and 6-membered heterocycles.[2] Study of such substrates for the obtention of larger ring sizes should give



Scheme 16

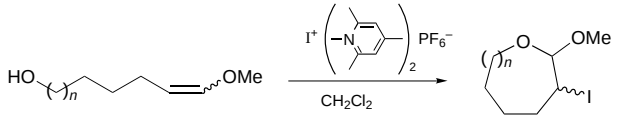


Scheme 17

interesting results (see for example the results reported in Section 3).

2.2 Formation of cyclic ethers by *endo*-mode cyclization

As we have seen in the Introduction, the presence of a highly carbocationic stabilising group on the carbon–carbon double bond can favour an *endo*-mode cyclization. For example, we found that the oxepanes were favoured over the more stable tetrahydropyrans if a methoxy group was fixed to the double bond. This *endo*-cyclization was also exclusively observed for the formation of oxocanes, however, in this case the ring closure was less efficient (Scheme 18).[9] We attribute this last result to



n = 1 84%

n = 2 23%

Scheme 18

the fact that introduction of a methoxy group (or another substituent) on the terminal carbon atom of the double bond is unfavourable, due to the increase in steric hindrance. This effect seems more pronounced for the formation of 8-membered ring heterocycles (and probably for the larger ring sizes) compared to smaller ring sizes.

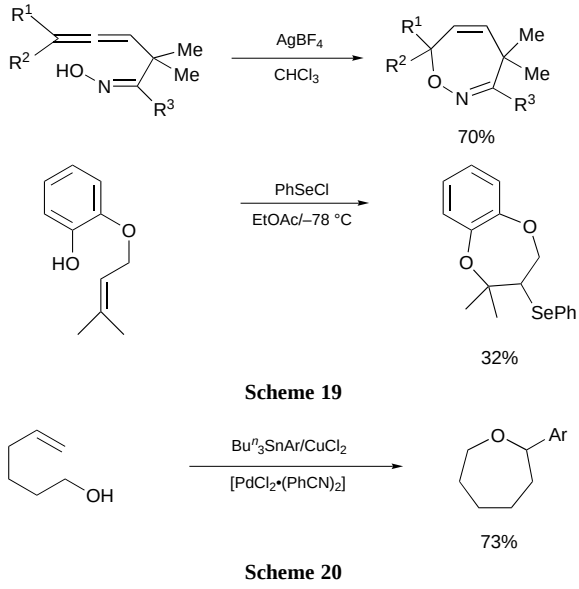
This substituent effect also seems to be responsible for the 7-*endo* cyclization of allenic derivatives, using silver tetrafluoroborate, instead of the more obvious 6-*exo* cyclization.[25] In the same way a 7-*endo* cyclization was observed for the reaction of a highly sensitive phenol with phenylselenochloride[26] (Scheme 19).

Palladium also appears to favour the *endo*-cyclization mode, since the oxepane was found as the unique product in the cyclization of hex-5-en-1-ol.[27] Unfortunately, the scope of this reaction was not examined (Scheme 20).

2.3 Formation of lactones

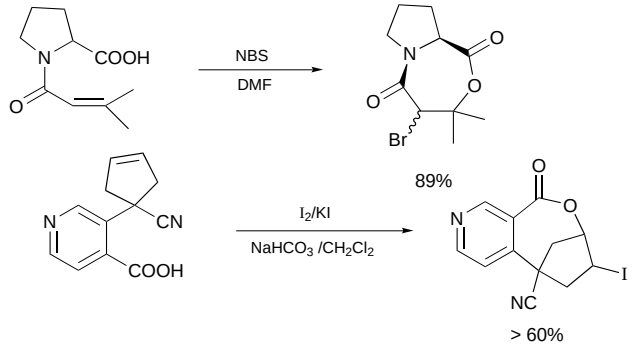
When we started our work in this field nothing was known about the possibility of preparing medium ring lactones (mediolides)† by an electrophilic cyclization. Only rare examples were reported concerning ε-caprolactones and large ring lactones. After several unsuccessful attempts,[3] the first ε-caprolactones were obtained from substrates possessing a certain rigidity brought by proline or benzo rings[28] (Scheme 21).

† We suggest the term mediolide for medium ring lactones, in comparison with macrolides for large ring lactones.



Scheme 19

Scheme 20



Scheme 21

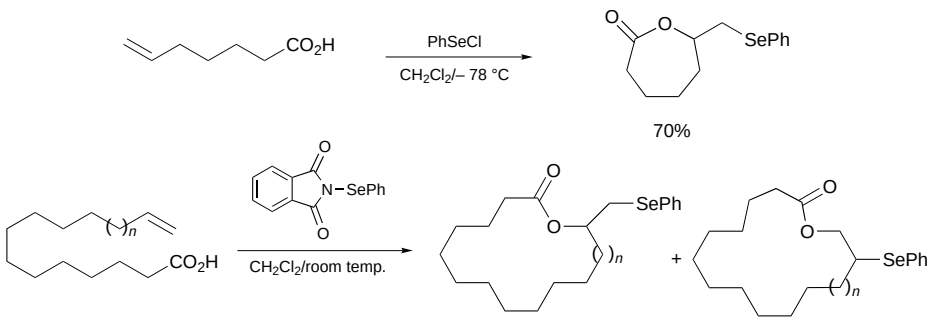
Reaction of phenylselenochloride with hept-6-enoic acid was reported to lead to ε-caprolactone. This reagent was inefficient for larger membered ring lactones. However, it was found that *N*-phenylselenophthalimide could be used to prepare large ring lactones (14 to 16) (Scheme 22).[29] In these conditions small amounts of the *endo*-cyclization products were isolated.

Important advances in this field were made using bis(collidine)iodine(I) hexafluorophosphate as the electrophile. In a first study we checked the reactivity of 4-oxahept-6-enoic acid with different iodine reagents. These results are summarised in Scheme 23.

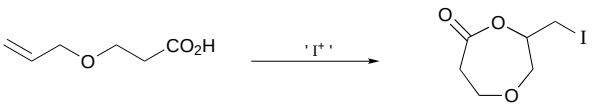
The superiority of $I^+(collidine)_2\ PF_6^-$ in this reaction (due to the very low nucleophilicity of the anion) led us to study the reactivity of this reagent with a wide range of unsaturated acids. While hept-6-enoic acids led in high yields to the corresponding ε-caprolactones, the results were much more disappointing for larger ring sizes. Indeed the 8- and 11-membered ring lactones were obtained in low yields (Scheme 24).[30]

We decided to examine which kind of structural modifications of the carbon chain would favour the cyclization. Three factors were examined : the oxygen effect, the *gem*-dimethyl effect and the influence of a carbon–carbon double bond.

The introduction of an oxygen atom in the carbon chain is known to favour the cyclization for numerous ring sizes.[37] However, an exception was noticed concerning the seven-membered heterocycles. In fact, this negative effect could be suppressed either by adding substituents on the carbon–carbon

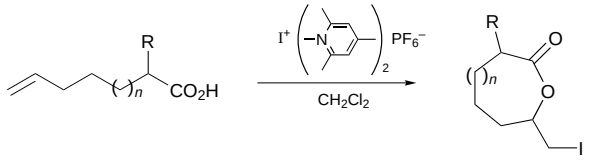


Scheme 22



I_2/CH_3CN	0%
ICl/CH_2Cl_2	0%
$NIS/AgOTf/CH_2Cl_2$	0%
$I^+(collidine)_2\ ClO_4^-/CH_2Cl_2$	24% (ref. 10)
$I^+(pyridine)_2\ PF_6^-/CH_2Cl_2$	20%
$I^+(collidine)_2\ PF_6^-/CH_2Cl_2$	59%

Scheme 23



n = 1, R = H	76%
n = 1, R = Me	49%
n = 1, R = Cyclohexyl	79%
n = 1, R = Bu^t	72%
n = 2, R = H	5%
n = 5, R = H	4%

Scheme 24

double bond or changing the position of the oxygen in the chain (Scheme 25).[30]

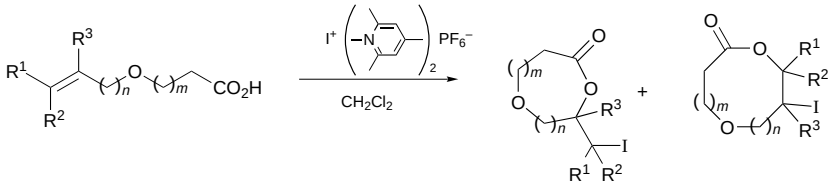
A positive oxygen effect was observed for the formation of larger ring sizes, since lactones in the range 8–13 were obtained in moderate yields. For these ring sizes a competition between the *exo*- and *endo*-cyclization was often observed (Scheme 26). Comparison of these results with those reported for the selenolactonization reaction (Scheme 22) shows that iodine favours the *endo*-cyclization mode.

We found that all these cyclizations occurred under kinetic control. This means that the decrease of CH···HC intramolecular non-bonding interactions used to explain the oxygen effect[31] is not a satisfactory one for these results. We suggested that the oxygen atom induces a stabilisation effect by formation of an intermediate. This stabilisation decreases the activation entropy of the reaction and consequently favours the cyclization.[30]

The *gem*-dialkyl effect is well known in the formation of five- and six-membered ring compounds.[32] We decided to carry out a study of this effect for the formation of ε-caprolactones and mediolides. For caprolactones almost no effect could be detected. However with mediolides a positive effect was observed, since 8–12 membered lactones were formed in moderate yields (Scheme 27). Here, a competition between the *exo* and *endo* cyclization was also established.[33]

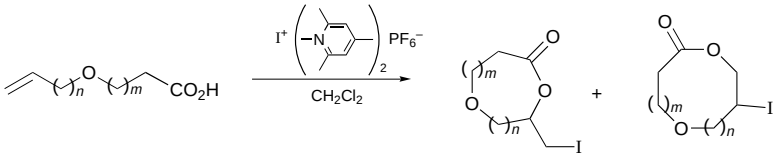
It seems obvious that the presence of an unsaturation on a chain should favour the formation of cyclic compounds. In our case we decided to study the reactivity of α,β-unsaturated acids. As reported in Scheme 28, the presence of a *cis* double bond favours the cyclization. For example, 8-membered lactones were obtained in exceptional yields.[34]

As we have previously noted, the proportion of *endo* cyclization increases appreciably with the lactone size. The beneficial effect of a *cis* double bond was also observed in the



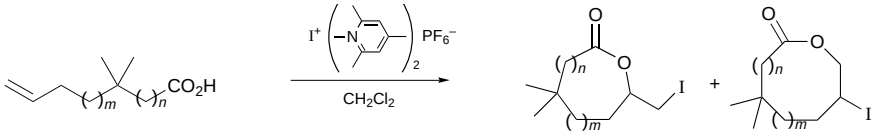
$m = n = 1$	R^1, R^2, R^3 = H	59%	-
$m = n = 1$	R^1, R^2 = H; R^3 = Me	70%	-
$m = n = 1$	R^1 = Me; R^2, R^3 = H	45%	45 %
$m = n = 1$	R^1, R^2 = Me; R^3 = H	5%	39%
m = 0, n = 2	R^1, R^2, R^3 = H	75%	-
m = 0, n = 2	R^1, R^2, = H; R^3 = Me	75%	-

Scheme 25



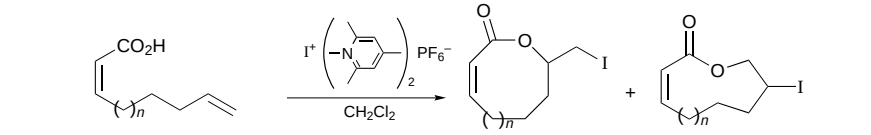
m = 0, *n* = 3	23%	23%
m = 1, *n* = 2	40%	5%
m = 2, *n* = 1	8%	-
m = *n* = 2	24%	24%
m = 0, *n* = 5	18%	18%
m = 0, *n* = 6	7%	21%
m = 2, *n* = 5	16%	16%

Scheme 26

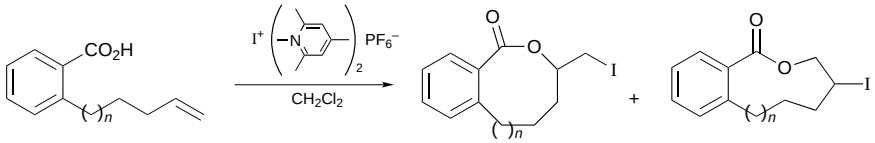


m = 3, *n* = 0	23%	-
m = 2, *n* = 1	41%	-
m = 1, *n* = 2	26%	17%
m = 3, *n* = 1	19%	-
m = 5, *n* = 1	23%	4%

Scheme 27



n = 1	80 %	-
n = 2	18 %	12 %
n = 3	10 %	10 %
n = 4	6 %	9 %



n = 1	83%	-
n = 2	40%	22%
n = 3	30%	30%
n = 4	20%	36%

Scheme 28

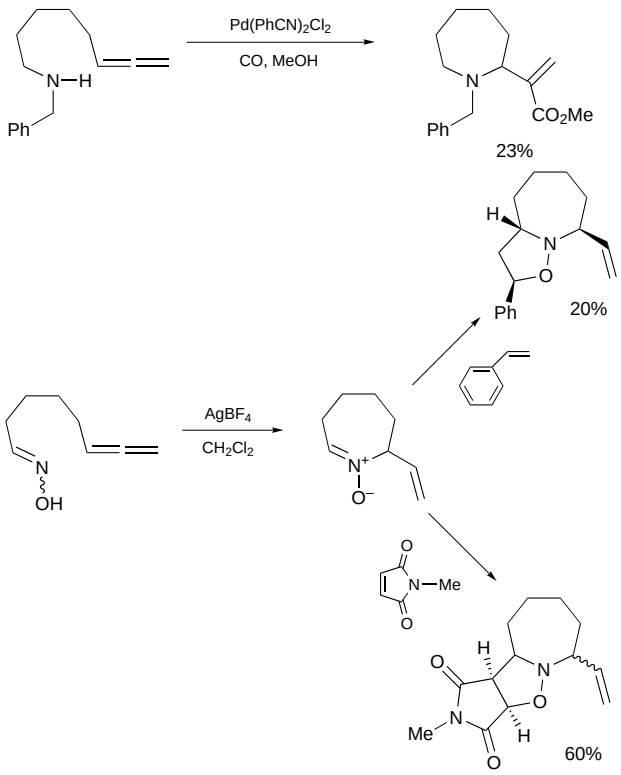
formation of an ε-caprolactone. In this case the yield was almost quantitative. The presence of a *gem*-dimethyl group on the terminal double bond explains the large proportion of *endo*-cyclization (Scheme 29).[35]

3 Nitrogen as nucleophile

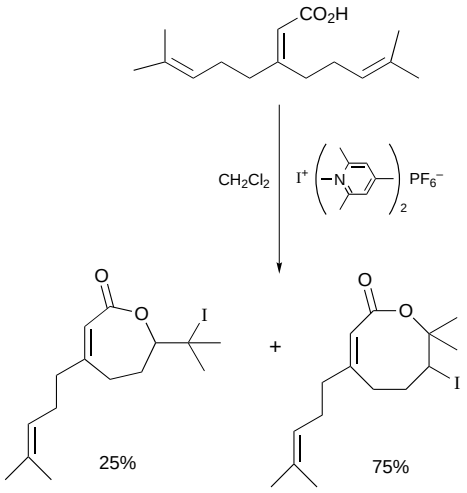
Currently, there are very few results concerning the possibility of preparing nitrogen heterocycles larger than six-membered rings by electrophilic cyclization. A hexahydroazepine was obtained using Pd^{II} salts as electrophiles. In this reaction, the presence of the allene unsaturation appeared necessary (Scheme 30).[36] With these substrates no reaction was observed in the presence of silver salts. However, starting from an oxime, the cyclization did occur in the presence of silver tetrafluoroborate, giving an unstable nitrone which could be trapped with different dienophiles.[36*a*]

Interestingly, the same authors found that these allenic substrates could lead to 7–11 membered azacycles in moderate yields using a two step reaction. Addition of iodine led to the diiodo products which were cyclized by slow addition to a NaH suspension (Scheme 31). The preference for the *endo* products was explained by the easier S_N2 substitution of the primary iodide compare to the $S_{N'}2$ substitution.[36*b*]

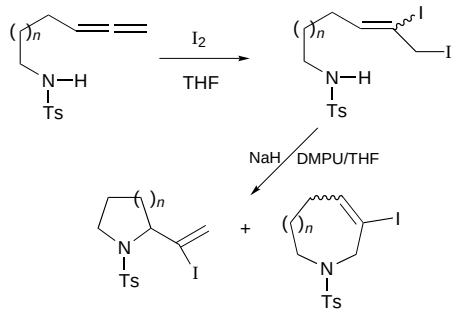
Recently, we investigated the possibility of preparing 8-membered ring lactams by halolactamization. The cyclization



Scheme 30



Scheme 29



n = 1	83%	10%
n = 2	22%	35 %
n = 3	-	55%
n = 4	-	62%
n = 5	-	35%

Scheme 31

did occur if a sulfone was fixed on the nitrogen atom to increase its nucleophilicity. We were able to obtain the azocanones in moderate yields (Scheme 32).[34] These results open new possibilities in this area, in particular for the preparation of azepanones.

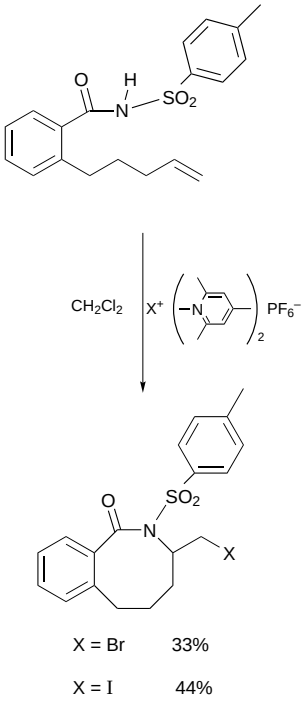
4 Conclusion

This article shows that contrary to what was previously thought, it is now possible to obtain heterocycles larger than 6-membered rings by electrophilic cyclization. As we have seen, several reagents are already available for the formation of 7-membered heterocycles. For larger membered heterocycles the situation is more critical. To have a successful cyclization one of the two criteria (or better both) must be fulfilled: (*i*) choice of the electrophile and (*ii*) choice of the substrate. For the moment few reagents are available and it appears necessary to design new ones. Indeed, the nucleophile part of the reagent should be non-reactive to avoid competition with the nucleophile part of the substrate. Also, it is necessay to modify the substrates to decrease the activation entropy of these reactions. This can be done either by formation of an intermediate chelate or by introduction of a steric restraint.

As we have seen in this review, depending on the R group present on the C-C double bond, and the nature of the electrophile, it is possible to orientate the cyclization to an *exo*-mode or an *endo*-mode. From our experimental results and following Baldwin's rules[37] we can add two complementary rules for ring sizes $\geqslant 7$.

Rule 1: for these ring sizes both the *exo* and *endo* cyclizations are favoured.

Rule 2: the *exo* to *endo* ratio decreases with increasing ring size. This phenomenon is more or less pronounced depending on the electrophile, and the substitution pattern.



X = Br 33%

X = I 44%

Scheme 32

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Received, 19th May 1997
Accepted, 14th July 1997