Tetrahedron Vol. 39, No. 5, pp. 703 to 731, 1983
Printed in Great Britain

0040-4020/83/050703-29$14.50/0
Pergamon Press Ltd.

TETRAHEDRON REPORT NUMBER 144

AMINATION OF ALKENES

M. B. GASC, A. LATTES and J. J. PERIE
Equipe de Recherches associée au CNRS n° 264, UER PCA, Université Paul Sabatier, Bat. IIR₁, 118, Route de Narbonne 31062 Toulouse Cedex, France

(*Received in the U.K.* 11 *May* 1982)

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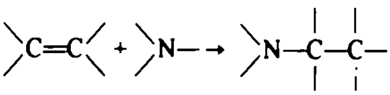
INTRODUCTION

Alkene amination occupies a particular position among the major organic synthetic methods since no general procedure can be used, the reaction conditions depending on the specific alkene or amine. However among the abundant literature covering the field (covered in this review to the end of 1981) some of these reactions lead to a functionalized carbon chain with fair to good yields and in some cases, stereospecifically. The aim of this report is to discuss the more significant results obtained with alkenes, including dienes and allenes, both as a synthetic tool and from a chemical reactivity point of view.

In order to limit this scope, more classical methods of amination such as Michael or Ritter reactions and reductive amination of other double bonds, are not considered since they have been described recently.[1,165] Moreover, allylic amination reactions are not included in this paper, except for cases where this reaction can compete with double bond amination.

Two ways can be used to make the following reaction feasible:



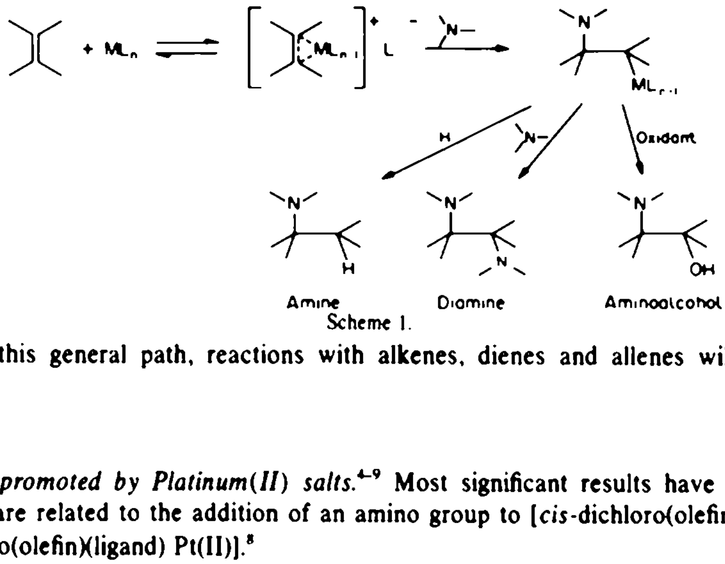
either to proceed to double bond activation by forming an olefinic complex with a metal, complex which then undergoes a nucleophilic attack by an amine, or making the amino group more electrophilic. These two approaches are successively considered in this report.

(A) AMINATION OF ACTIVATED DOUBLE BONDS

I. *Activation by metallation*

One first recalls that metal addition to a double bond creates a π complex, which according to the classical model of Dewar–Chatt–Duncanson, contains two types of bonding: π-bonding from olefin to metal and $d\pi \rightarrow \pi^*$ back-donation from metal to olefin. The stability of this complex and therefore its transformation to a σ-adduct by nucleophilic addition (e.g. amine) depends largely on the back donation term, the later being also under the control of the ligands around the metal.[2,3]

The second step, from the metallated intermediate to functionalized product, can be achieved in different ways and leads to an amine, a diamine or an aminoalcohol, depending upon the experimental conditions used for the demetallation step (Scheme 1).



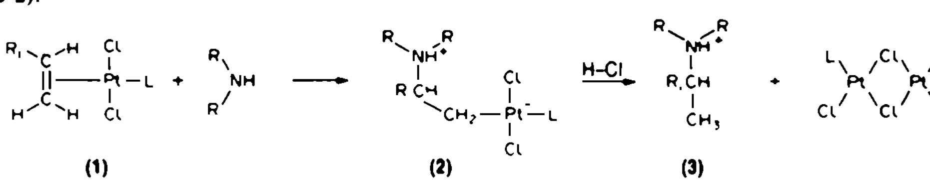
Scheme 1.

According to this general path, reactions with alkenes, dienes and allenes will be successively considered.

1. *Alkenes*

1.1 *Additions promoted by Platinum(II) salts.*[4–9] Most significant results have been obtained by Paiaro *et al.* and are related to the addition of an amino group to [*cis*-dichloro(olefin)(ligand) Pt(II)][4–7] and [*trans*-dichloro(olefin)(ligand) Pt(II)].[8]

Addition of an amine to complex (1) leads to compound (2) (Scheme 2), whose zwitterionic structure has been established by X-ray analysis. NMR techniques follow the change from π- to σ-bonding (Scheme 2).[7]



(1) (2) (3)

R H, CH3, C2H5
R2 CH3, C2H5, C4H9
L phosphine

R_1	R_2	Yields of (3)(%)
H	CH_3	68
H	C_2H_5	62
H	C_4H_9	55

Scheme 2.

For propylene and l-butene, in which two non-equivalent sites of addition are present, tendency to consecutive alkylations leads to mixtures of different amines; no result is obtained with aromatic amines.

These reactions are weakly regioselective, the predominant pathway being directed by the *cis* ligand relative to olefin around the metal.[7]

1.2 *Additions promoted by palladium(II) salts.*[10–23] This route has been widely developed and reviews on the topic have recently been published.[10,11]

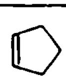
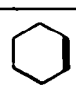
Yields are poor for the first examples of such a reaction given in the literature,[12,13] but improvements have been then obtained by Akermark *et al.* using the bis(benzonitrile)$PdCl_2$ complex.[14] Indeed it gives weak adducts with amines compared to the other Pd(II) salts previously used, limiting this competitive reaction. Principal results given in Table 1 show that regioselectivity depends on amine and olefin; for a given α-olefin, amination proceeds on the β atom if the amine is sterically free, and on the α carbon with amine bearing bulky groups; for a given amine, yield for addition on the terminal olefinic carbon is better for 1-decene than for 1-butene; relative reactivities are *trans* better than *cis* and α-alkene better than corresponding internal double bond.

The following reaction scheme (Scheme 3) is suggested[14] to account for the stoichiometry (three moles amine per mole olefin) and the *trans* stereochemistry as shown with 2-butenes.[15]

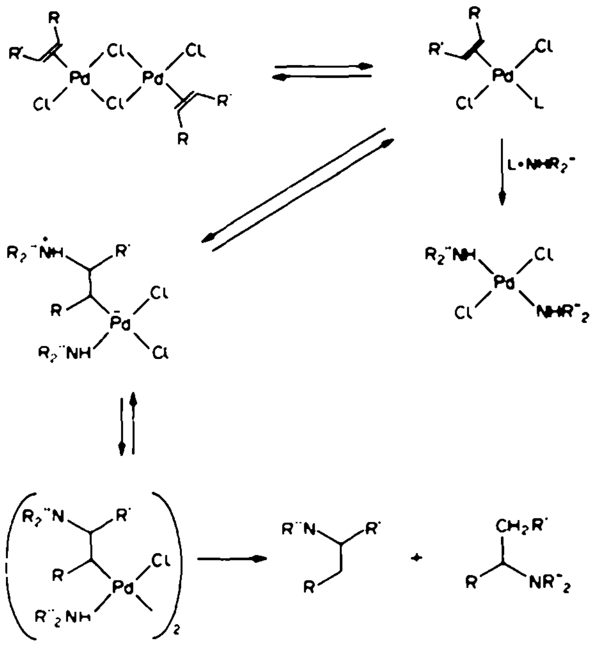
The higher reactivity of *trans*-2-butene over *cis*-2-butene (by 18:1) in competitive palladium promoted amination of butenes[16] implies that the stability of these π-alkene complexes strongly affect the relative rates; the free energy of *cis*-2-butene palladium complex must be lower than that of *trans*-2-butene.

Alkenes are transformed in a "one pot" reaction to vicinal amino–alcohol derivatives by an oxidative cleavage of the metal–carbon bond in the β-aminopalladium σ complex (compound **4** in Scheme 3).[17,18] Among the oxidants used, lead tetraacetate $Pb(OAc)_4$ is the most efficient for dimethylaminoadducts.

Table 1. Alkenes amination promoted by palladium (bis(benzonitrile)$PdCl_2$)

Olefin	Amine	T°c	Isomer A/M	Yield(%)
$CH_2{=}CHCH_2CH_3$	$(CH_3)_2NH$	20		16
	$(CH_3)_2NH$	-60	1/7	90
	$((CH_3)_2CH)_2NH$	-50	> 20/1	3
	CH_3NH_2	-50	1/4	40
	NH_3	-50	1/3	4
$CH_2{=}CH(CH_2)_7CH_3$	$(CH_3)_2NH$	-50	1/4.5	90
	$((CH_3)_2CH)_2NH$	-50	> 20/1	6
	CH_3NH_2	-50		40
trans-$CH_3CH{=}CHCH_3$	$(CH_3)_2NH$	-50		44
cis-$CH_3CH{=}CHCH_3$				15
trans-$CH_3CH{=}CH(CH_2)_4CH_3$	$(CH_3)_2NH$	-50	1/1.5	66
cis-$CH_3CH{=}CH(CH_2)_4CH_3$			1/1.8	24
	$(CH_3)_2NH$	-50		62
	$(CH_3)_2NH$	-50		traces
	$(CH_3)_2NH$	-50		none

*M = Markownikov isomer; A = anti-Markownikov isomer.



(4)

Scheme 3.

Terminal olefins give good yields (60–80%), internal alkenes lower (20–60%). Some results are given in Table 2.

Also, similar reactions using primary amines followed by bromine oxidation result in the formation of N-substituted aziridine.[19]

This oxyamination reaction is stereospecific and proceeds by an overall *cis* stereochemistry: *trans*

Table 2. Palladium promoted oxyamination of olefins

Olefin	Amine	Oxidant	Aminoacetate or Aminoalcohol	Yield(%)
$CH_2=CH_2$	$(C_2H_5)_2NH$	NBS	$(C_2H_5)_2NCH_2CH_2OAc$	50
$CH_2=CHCH_2CH_3$	$(CH_3)_2NH$	$Pb(OAc)_4$	$C_2H_5CH(N(CH_3)_2)CH_2OH$ (88) $C_2H_5CH(OH)CH_2N(CH_3)_2$ (12)	84
$CH_2=CHCH_2CH_3$	$C_6H_5CH_2NHCH_3$	NBS	$C_2H_5CH(N(CH_3)CH_2C_6H_5)CH_2OAc$ (53) $C_2H_5CH(OAc)CH_2N(CH_2C_6H_5)CH_3$ (47)	62
$CH_2=CH(CH_2)_3CH_3$	$(C_2H_5)_2NH$	$Pb(OAc)_4$	$CH_3(CH_2)_3CH(N(C_2H_5)_2)CH_2OAc$ (43) $CH_3(CH_2)_3CH(OAc)CH_2N(C_2H_5)_2$ (57)	44
$CH_2=CH(CH_2)_3CH_3$	$(C_2H_5)_2NH$	Br_2	$CH_3(CH_2)_3CH(N(C_2H_5)_2)CH_2OAc$ (47) $CH_3(CH_2)_3CH(OAc)CH_2N(C_2H_5)_2$ (53)	32
$CH_2=CH(CH_2)_3CH_3$	$(C_2H_5)_2NH$	NBS	$CH_3(CH_2)_3CH(N(C_2H_5)_2)CH_2OAc$ (42) $CH_3(CH_2)_3CH(OAc)CH_2N(C_2H_5)_2$ (58)	71
$CH_2=CH(CH_2)_7CH_3$	$(CH_3)_2NH$	$Pb(OAc)_4$	$CH_3(CH_2)_7CH(N(CH_3)_2)CH_2OAc$ (84) $CH_3(CH_2)_7CH(OAc)CH_2N(CH_3)_2$ (16)	80
$C_6H_5CH=CH_2$	$(C_2H_5)_2NH$	NBS	$C_6H_5CH(OAc)CH_2N(C_2H_5)_2$	61

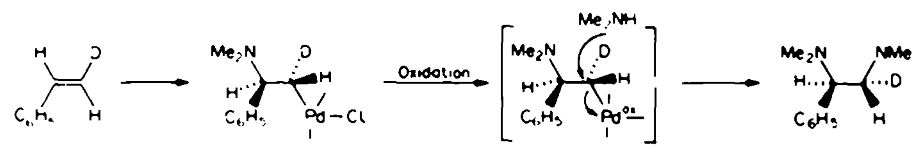
Table 3. Diamines synthesis by amination/oxidation of alkenes

Olefin R'CH=CHR"	Oxidant	Diamine Yield (%) R'CH(N(CH$_3$)$_2$)CH(N(CH$_3$)$_2$)R"
CH_2=CH_2	Br_2	60
CH_2=$CHCH_2CH_3$	Br_2	70
trans-CH_3CH=$CHCH_3$	MCPBA	45 (95% threo)
CH_2=$CH(CH_2)_3CH_3$	MCPBA	77
CH_2=$CH(CH_2)_7CH_3$	Br_2	70
CH_2=$CH(CH_2)_7CH_3$	MCPBA	81
CH_2=$CH(CH_2)_7CH_3$	$Pb(OAc)_4$	60
C_6H_5CH=CH_2	MCPBA	87

aminopalladation then followed by an oxidative cleavage of the palladium–carbon bond with inversion of configuration at carbon.

Olefins can also be stereospecifically transformed into vicinal diamines by an aminopalladation-oxydation sequence using oxidant such as bromine, m-chloroperbenzoic acid (MCPBA), and N-bromosuccinimide (NBS). Results in Table 3 show that terminal olefins are diaminated in good yields.[20]

The diamination process is an overall *cis* process (more than 90% *cis* addition) as represented in Scheme 4:



Scheme 4.

Palladium activation has also been used to promote intramolecular amination of double bond, orthoallylanilines for instance being transformed to indoles with good yields;[21,22] the reaction was then applied to electron-deficient alkenes.[23]

1.3 *Additions promoted by rhodium and iridium salts.*[24] Metal salts such as $RhCl_3$, $3H_2O$ or $Rh(NO_3)_3$; $IrCl_3$, $3H_2O$ are good catalysts for addition of secondary amines to ethylene. This reaction (restricted to ethylene) is sensitive to bulkiness on amine, and also to its nucleophilicity as shown on Table 4.

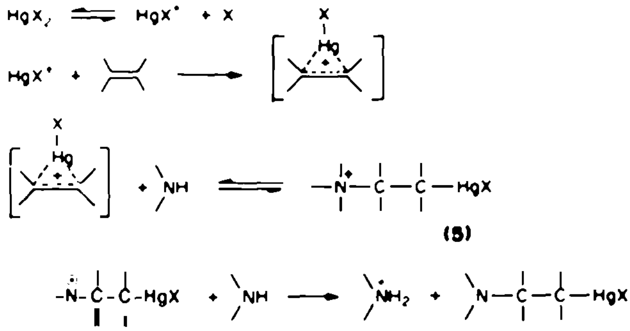
1.4 *Additions promoted by mercury (II) salts.*[25–44] Proposed for the first time in 1945,[25] amine addition on an alkene activated by a mercuric salt has been since extensively developed in the authors' laboratory.[26–32]

The reaction is described in following Scheme 5. To these steps is added the competitive reaction between amine and mercury salt:

$$HgX_2 + \rangle NH \rightleftarrows (X\,Hg \cdot NH)^+ X^- \quad (6)$$

(6)

The formation of complex **6** (soluble if the solvent used is the amine itself) limits the reaction since decreasing the concentration into the active species HgX^+. For aromatic amines, which give stable



Scheme 5.

complexes, specific reaction conditions can be used to overcome this limitation; the reaction is carried out in mixed solvent: THF/H_2O (water was initially ruled out to avoid competitive oxymercuration[33]); in fact water is required for the reaction of the transitory aromatic ring mercuration step. The consequence of this ring mercuration is to decrease amine basicity and therefore to weaken the stability of the complex **6**. This point has been clearly shown by UV technique.[31] Oxymercuration does not interfere if water is added after the alkene.

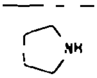
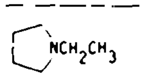
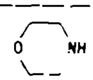
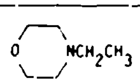
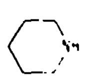
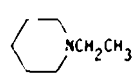
The step from the organomercury intermediate **5** to amine is achieved by cleavage of the carbon-mercury bond with an hydride; rearrangement initially observed in the hydrogenolysis step[29] is avoided by using phase transfer conditions.[32] The whole reaction is therefore regiospecific (nitrogen is attached at the β-carbon of a terminal olefin) the first step being a stereospecific *trans* process.[30,34]

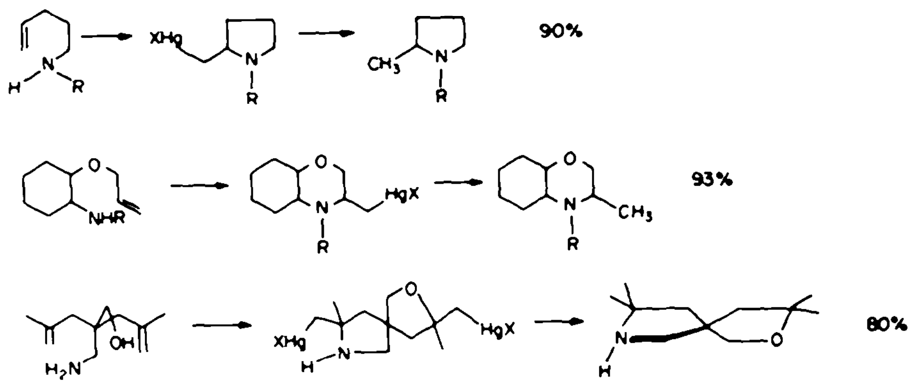
Examples of this reaction are given in Table 5. Similar reactions have been extended to functionalized olefins.[35]

$$CH_3CH{=}CHCH_2OH \xrightarrow[(2)\ NaBH_4,\ OH^-]{(1)\ C_6H_5NH_2,\ Hg(OAc)_2,\ THF/H_2O} C_6H_5NH{-}\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2OH$$

The same reaction in an intramolecular scheme with substrates of structures $CH_2{=}CH(CH_2)_4NHR$ led to the development of a general synthetic method of heterocycles; different examples have been published,[36-38] and a few cases are given in Scheme 6.

Table 4. Ethene amination promoted by rhodium(III) salts

Amine	Product	Yield(%)	pKa of amine
$(CH_3)_2NH$	$(CH_3)_2NCH_2CH_3$	54	10.7
$(C_2H_5)_2NH$	$(C_2H_5)_3N$	4	10.5
$CH_3(CH_2)_3NH(C_2H_5)$	$CH_3(CH_2)_3N(C_2H_5)_2$	3	10.5
		36	11.3
		2	8.3
		70	11.[illegible]

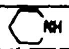
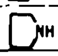
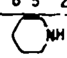
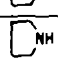
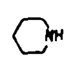
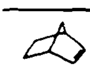


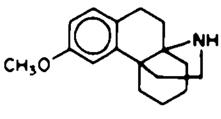
Scheme 6.

Later developments have been given to this reaction, for example synthesis of methoxy-3 hasubanane 7[39] (a morphine analogue), and heterocyclisation through a nitrogen atom of an aziridino group[40] (Scheme 7).

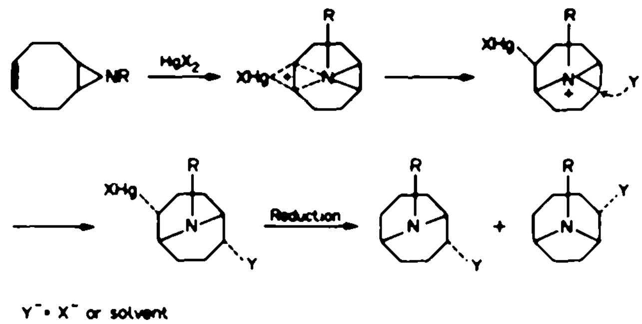
A new synthesis of aromatic diamines using the same general process has also been developed;[41]

Table 5. Double bond amination via mercuric salts

Amine	Olefin	Solvant	HgX_2	N-Alkylation product Yield(%)
	$CH_2=CH_2$	amine	$HgCl_2$	60
	$CH_2=CH_2$	amine	$HgCl_2$	70
$C_6H_5NH_2$	$CH_2=CH_2$	THF	$HgCl_2$	40
$C_6H_5NH_2$	$CH_2=CH_2$	THF	$Hg(OAc)_2$	43
	$CH_2=CHCH_3$	amine	$HgCl_2$	55
	$CH_2=CHCH_3$	amine	$HgCl_2$	45
$C_6H_5NH_2$	$CH_2=CHCH_3$	THF	$HgCl_2$	30
	$C_6H_5CH=CH_2$	amine	$HgCl_2$	60
	$C_6H_5CH=CH_2$	amine	$HgCl_2$	65
$C_6H_5NH(CH_3)$	$C_6H_5CH=CH_2$	THF	$Hg(OAc)_2$	50
	$CH_2=CHCH_2CH_3$	amine	$HgCl_2$	none
	$CH_3CH=CHCH_3$	amine	$HgCl_2$	none
	$CH_2=C(CH_3)_2$	amine	$HgCl_2$	70
		amine	$HgCl_2$	none
		amine	$HgCl_2$	40
$C_6H_5NH_2$		THF/H_2O	$Hg(OAc)_2$	37
$C_6H_5NH_2$		THF/H_2O	$Hg(OAc)_2$	(exo) 35
$C_6H_5NH_2$	$CH_3(CH_2)_nCH=CH_2$	THF/H_2O	$Hg(OAc)_2$	n=4,80;n=5,47 n=9,40
$C_6H_5NH_2$	$C_6H_5CH=CH_2$	THF/H_2O	$Hg(OAc)_2$	50



(7)



Scheme 7.

instead of a hydride, an amine is used in the demetallation step. For instance:

$$CH_3CH{=}CH_2 + C_6H_5NH_2 \xrightarrow{HgO.\,HBF_4} CH_3CH(NHC_6H_5)CH_2HgBF_4$$

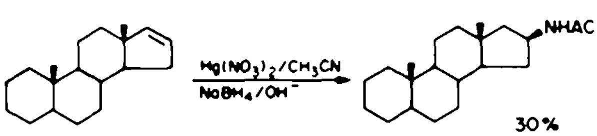
$$\downarrow C_6H_5NH_2$$

$$CH_3CH(NHC_6H_5)CH_2NHC_6H_5 \quad 62\%.$$

Other yields are in the range 80–90% with styrene or allylbenzene.

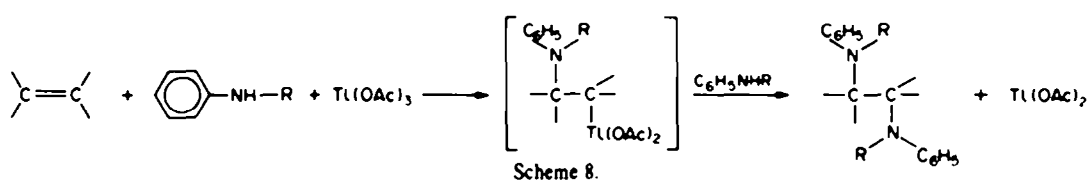
This process was recently extended to synthesis of amino-amidines starting with acetylenic aminoalcohols.[42]

Other nucleophiles than amines can also be used such as azide,[43] amides,[44] or nitrile[45] for which the following example is given:



These last examples are akin to alkene amination since the products can be easily transformed to amine.

1.5 *Additions promoted by thallium(III) salts.*[46,47] Amination has also been carried out with thallium acetate, $Tl(OAc)_3$, by Aranda *et al.*[46] according to Scheme 8.



Scheme 8.

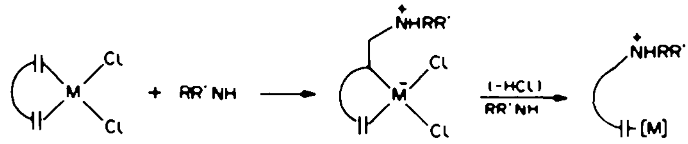
Aromatic diamines are obtained with good yields as shown in Table 6. Similar reactions were also performed starting with phenylacetylene, the products being imines or enamines depending on nitrogen and ring substitutents of the aromatic amine used.[47]

2. *Dienes*

2.1 *Additions promoted by mercury(II) salts.*[48–51] Amination of non conjugated dienes through mercuration was first described by Aranda,[48] then investigated in more details by present authors,[49] particularly as a model of mercuration in micellar conditions. Results given in Table 7 show that significant improvements can be obtained in this way.[50]

2.2 *Additions promoted by palladium(II) and platinum(II) salts.*[4,52–57] Along a similar reaction path to that proposed for monoolefins, ammonia and aliphatic amines react with nonconjugated dienes bound to metal affording a σ compound **9**[4,52–54] as shown in Scheme 9.

For platinum, intermediate (**8**) can be isolated if the diene chain is long enough (1,5-diene for instance). Further hydrogenolysis of the carbon–metal bond gives the amine with some amounts of retroamination.[55,56] Examples are given in Table 8.



M Pd(II), Pt(II) **(8)** **(9)**

Scheme 9.

Table 6. Diamines synthesis promoted by thallium salts

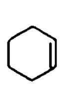
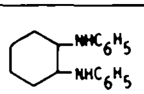
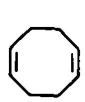
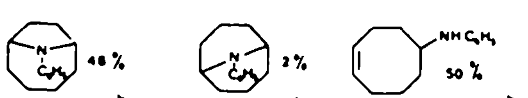
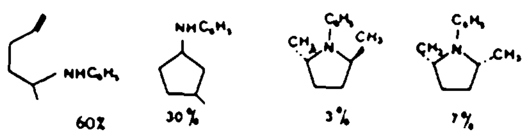
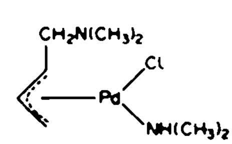
Olefin	product	Yield(%)	T°c
$CH_2{=}CH_2$	$C_6H_5NHCH_2CH_2NHC_6H_5$	81	70
$CH_2{=}CHCH_3$	$C_6H_5NHCH_2CH(CH_3)NHC_6H_5$	85	70
$C_6H_5CH{=}CH_2$	$C_6H_5NHCH_2CH(C_6H_5)NHC_6H_5$	68	75
		50	100

Table 7. Products of dienes amination by aniline

Diene	Product after demercuration step	Overall Yield(%)
	 60%[b] 10%[b] 30%[b]	50
	 60% 30% 3% 7%	45
	15%[a] 10%[a] 75%[a]	60[a]

[a]In H_2O/SDS.
[b]Same reaction described by Barelle *et al.*[51]

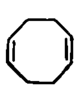
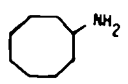
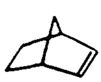
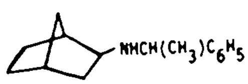
The same reaction relative to butadiene has been studied in detail.[57] A first π-allylic complex **10** formed between butadiene, bis[benzonitrile]palladium dichloride and amine is then reacted with a second molecule of amine (after treatment with $AgBF_4$ or triphenylphosphine, this ligand exchange being required for aminolysis to proceed) leading then to 1,4-diamines.



(10)

2.3 *Telomerisation of* 1,3-*dienes promoted by palladium,*[59–65], *nickel*[65–73] *and rhodium salts.*[63,72] This well-known telomerisation reaction of dienes, catalysed by a metal,[58] can also be performed in the

Table 8. Palladium and platinum promoted amination of dienes

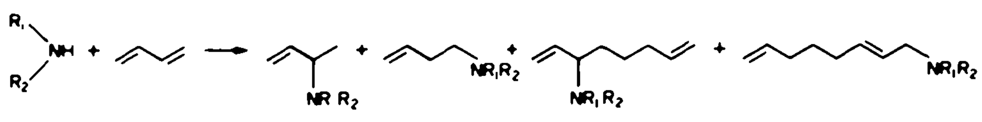
Diene	Amine	Product	Yield(%)	ref.
$CH_2{=}CH(CH_2)_2CH{=}CH_2$	NH_3	$CH_3(CH_2)_3CH(CH_3)NH_2$	93	53
	$(C_2H_5)_2NH$	$CH_3(CH_2)_5N(C_2H_5)_2$	92	53
	$C_6H_5CH(CH_3)NH_2$	$CH_3(CH_2)_5NHCH(CH_3)C_6H_5$	88	53
$CH_2{=}CHCH{=}CH_2$ [a]	$(CH_3)_2NH$	$CH_2(N(CH_3)_2)CH{=}CHCH_2N(CH_3)_2$	69	57
	NH_3		57	53
	$C_6H_5CH(CH_3)NH_2$		45	53

[a]Using 2 equiv. of $AgBF_4$; this yield is 84% if the reaction mixture is kept at r.t. for 24 h.

presence of ammonia or amine. This reaction can be a valuable method for long chain amine synthesis, the primary products (e.g. mixture of ethylenic amines) being then transformed to saturated compounds.

Palladium catalysts are either Pd(0) complexes such as $Pd[P(C_6H_5)_3]_4$, $Pd[P(C_6H_5)_3$, quinone] or Pd(II) salts. Selectivity for 1/1 adducts (one mole of amine per mole of diene) is improved by using protic solvent[60,65] or bidentate ligands such as diphosphines;[63] these reactants add to the metal center and therefore reduce vacant sites available for further binding of an other molecule of diene, responsible for telomerisation.

Interesting results have been obtained (as indicated in Scheme 10) when similar reaction is performed with nickel complexes.[69] The catalyst used in this reaction is a Ni(O) complex[69] formed *in situ* between Ni(II) acetylacetonate salts, a phosphine, and sodium borohydride. The function of the latter might be to participate to Ni(II) reduction in Ni(O)—a common feature to these telomerisation catalysts—as does trifluoroacetic acid according to Kiji *et al.*[65]



(11) (12) (13) (14)

Amine	Products, yields (%)				Overall yield (%)
	(11)	(12)	(13)	(14)	
Morpholine	15	32	2	51	96
Pyrrolidine	56	17	2	37	96
N-butylamine	100		Trace		31
P-anisidine	63	20	1	4	64

Scheme 10.

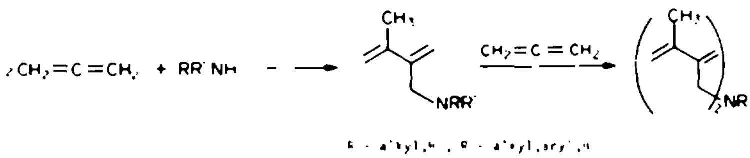
Baker[69] suggested a *trans* attack of the amine on a π-allyl (later caracterized by Kiji *et al.*[72]) and a π-bis allyl nickel(O) complex respectively, to account for 1/1 (e.g. **11** and **12**) and 1/2 (e.g. **13** and **14**) products.

As previously indicated for Pd catalysts, predominant formation of 1/1 adducts is favoured by use of hydroxylic solvent[68] and excess of phosphine, for the same reason. In opposite, use of preformed catalysts allows formation of 1/2 adducts with a selectivity higher than 85%, probably due to a possibility of binding of a second molecule of diene on to the metal. Later Baker and Halliday extended these reactions to rhodium complexes.[74]

3. *Allenes*

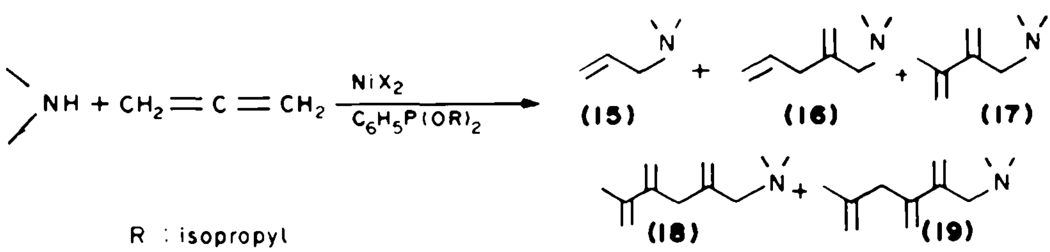
Much less work has been devoted to 1,3-diene amination, but results are similar to those obtained for other dienes. Mixture of products is formed, depending upon reaction conditions and structure of the reactants (particularly amines). However valuable procedures for specific cases are made available.

3.1 *Additions promoted by palladium and rhodium salts.* Coulson showed that several Pd(O), Pd(II) or Rh compounds catalyse addition of amines on allenes affording 1/2 adducts according to Scheme 11.[75] Palladium catalysts are more efficient than rhodium complexes for this reaction.



Scheme 11.

3.2 *Additions promoted by nickel(II) salts.* Baker extended the reaction described with dienes to allenes according to the following reaction.[76] Again the selectivity depends upon the structure of the amine used, as shown in Scheme 12.

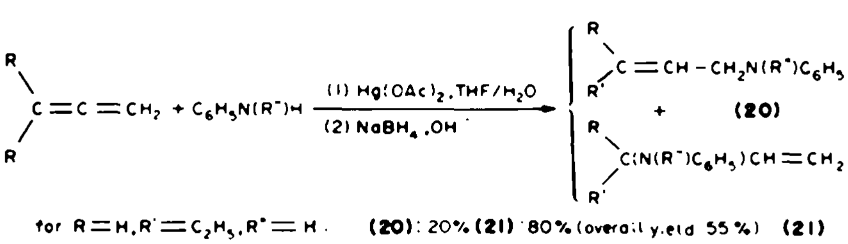


Amine	Products, yields (%) (15)	(16)	(17)	(18)	(19)	Overall yield (%)
Morpholine			22	5	73	100
N-butylamine		36	17	15	32	40
Aniline			20	25	55	16

Scheme 12.

These reactions which are of valuable synthetic interest with basic amines lead to predominant formation of **19**. This product results from addition of one mole amine to three moles allene, contrarily to what is obtained with rhodium or palladium. This interesting specific reactivity has been rationalized on the grounds of a greater stability of a bis-allyl nickel complex compared to that of monoallyl.

3.3 *Additions promoted by mercury salts.* Aminomercuration carried out in THF/H_2O mixture (as indicated before) allows amination of allenic compounds by aromatic amines to afford ethylenic amines.[49] The reaction is Scheme 13 for instance is easily carried out.



Scheme 13.

The mercury(II) intermediate is unique as determined by NMR. The mercury atom is fixed to the central carbon atom and the nitrogen to the most substituted one. The rearrangement observed during demercuration step can be suppressed by using phase transfer conditions; in this case the overall yield is improved to 70%.[32]

3.4 *Additions promoted by platinum salts.* Results obtained by Panunzi *et al.* have to be mentioned;[77] aliphatic, and also aromatic amines, react on 1,1-dimethylallene complexed to platinum to give zwitterionic alkenyl derivatives of the type *cis* $[P\bar{t}Cl_2(CH_3C{=}C(CH_3)\overset{+}{N}R_1R_2R_3)L]$ (with L:$P(C_6H_5)_3$; $As(C_6H_5)_3$; paratoluidine and DMSO). The structure of such complexes, established by X-ray analysis, reveals that allene coordinates through the less substituted double bond. On treatment with hydrogen chloride they afford the ammonium salts $[NR_1R_2R_3(CH_3CH{=}C(CH_3)_2]^+Cl^-$. Results depend on the bulkiness of the amine, but this work has not been directed to synthetic aspects.

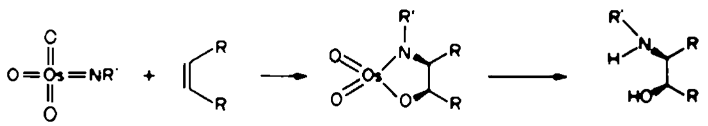
II. *Other methods*

Based on reactivity of osmium and sulpho/seleno compounds respectively towards double bonds, amination methods have been developed leading to different kinds of functionalized amines.

1. *Osmium derivatives*[78-85]

Sharpless *et al.* developed such synthetic routes to vicinal aminoalcohols,[78-82] hydroxycarbamates,[83,84] and vicinal diamines[85] using osmium salts.

Stoichiometric amounts of tert-alkylimido osmium compounds such as **22** react with different olefins to afford, after reductive cleavage of the osmate ester **23**, generally performed with $LiAlH_4$, vicinal tertiary aminoalcohols **24**. Yields are good to excellent; in some cases vicinal diol can be formed as by-product. Significant examples of this reaction are given in Table 9.



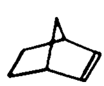
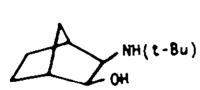
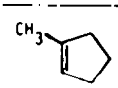
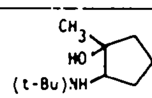
(22) **(23)** **(24)**

R' : tBu, adamantyl

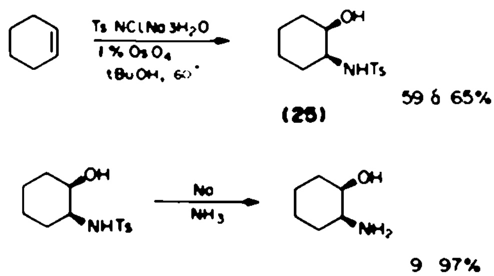
Scheme 14.

The synthetic utility of this new reaction was evaluated by investigating the effects of temperature, alkene substitution patterns and solvent.[79] It emerges that the stereochemistry of addition (in CH_2Cl_2 or pyridine) is exclusively *cis*; the new carbon–nitrogen bond formed is in every case formed at the least substituted olefinic carbon atom; di- and tri-substituted olefins react slower with imido reagent than do

Table 9. Oxyamination of alkenes catalysed by osmium salts

Alkene	Amino-alcohol yield(%)		1,2-diol yield(%)	Solvent
$C_6H_5CH{=}CH_2$	$C_6H_5CH(OH)CH_2NH(t\text{-}Bu)$	92 37	< 1 trace	pyridine CH_2Cl_2
$CH_2{=}CH(CH_2)_7CH_3$	$(t\text{-}Bu)NHCH_2CH(OH)(CH_2)_7CH_3$	89	< 1	pyridine
$C_6H_5C(CH_3){=}CH_2$	$(t\text{-}Bu)NHCH_2C(OH)(CH_3)C_6H_5$	93	< 1	CH_2Cl_2
$(CH_3)_2C{=}C(CH_3)_2$	none		81	pyridine
		94		pyridine
		66		pyridine

monosubstituted alkenes. Tetrasubstituted alkenes (e.g. 2,3-dimethyl 2-butene) yield only the corresponding diol); consistently, higher yields of aminoalcohols and higher ratios of aminoalcohol to diol are obtained with use of a coordinating solvent such as pyridine; coordination of the solvent to the metal centre is implied along the reaction pathway, as indicated by the fact that the yield in aminoalcohol is still enhanced by using bridgehead amines (e.g. quinuclidine) which binds to the metal more tightly than does pyridine;[80] and this process can be catalytic in osmium by use of chloramine T (TsNClNa) for the *in situ* regeneration of the imido osmium species.[81,82] An example of this reaction carried out with cyclohexene is given below.

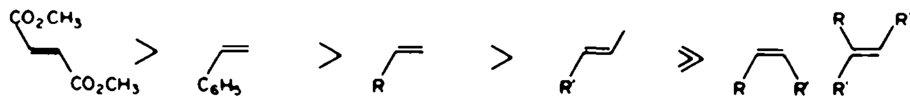


Compound **25** has then to be elaborated into a primary amine. This aminoalcohol synthesis is again an overall *cis* process. Improvements of this catalytic process have been obtained by using phase transfer catalyst,[82] addition of silver nitrate,[82] use of N-chloro-N-argentocarbamate generated *in situ*, instead of the chloramine T.[83] This process gives oxyamination products bearing protecting group (such as t-BOC or BOC) on the nitrogen atom. Use of different kinds of N-chloro-N-argentocarbamate in conjunction with the addition of Et_4NOAc to the reaction mixture is also beneficial. The highest reactivity is achieved[84] using RO–CO–NClNa (1.5 eq), $Hg(NO_3)_2$ (0.75 eq) and Et_4NOAc (1.0 eq). These results increase the utility of this oxyamination pathway, but this reaction has limitations; all the procedures described fail with tetrasubstituted alkenes; moreover the regioselectivity (with 1-alkenes) is lower than with procedure using a stoichiometric amount of osmium.

Similarly, dioxobis(tert-butylimido)osmium **26** and oxotris(tert-butylimido)osmium **27** compounds react with olefins to give primarily *cis* vicinal diamines.[85] With complex **27**, the ratio of diamines to

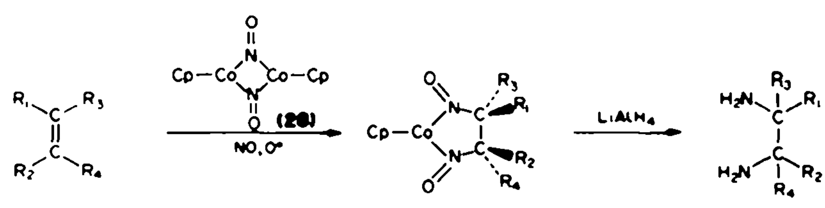
(26) (27)

aminoalcohol (by-product) is much better than with **26**. The relative reactivities of **26** and **27** towards differently-substituted alkenes are as follows.



2. *Cobalt derivatives*

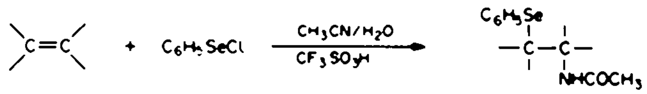
Recently Bergman *et al.*[86] report a new vicinal diamination of alkenes using cobalt-based reagent such as **28** according to Scheme 15. This reaction is quite general; complex **28** works satisfactorily with terminal, E and Z di-, tri- and at least some tetrasubstituted alkenes.



Scheme 15.

3. *Seleno and sulpho derivatives*[87-90]

Seleno and sulpho compounds have recently been used to effect allylic amination of olefins,[87] 1,2-diamination of 1,3-dienes,[88] promoted by selenium diimides species, TsN=Se=NTs; and 1,2-*trans* aminoselenation of alkenes.[89,90] Phenylselenyl chloride **29** reacts with olefin in acetonitrile containing small amounts of organic acid and water to give β-acetamidoalkyeselenide **30** in good to excellent yield (Scheme 16).[89]

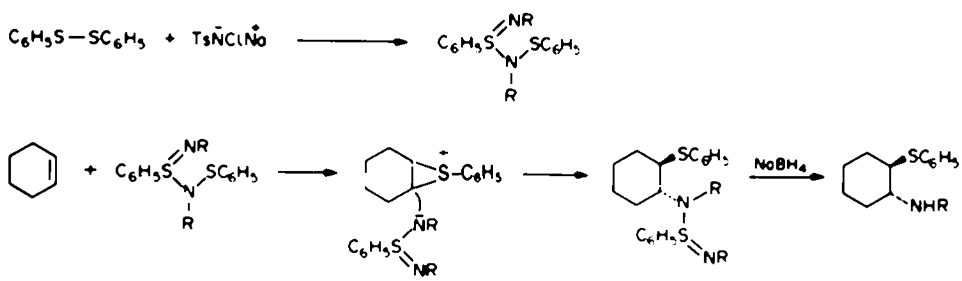


(29) **(30)**

	Yields (%)
1-hexene	74 (83 17)
trans-2-butene	70
cis-2butene	75
Cyclohexene	98

Scheme 16.

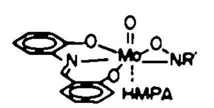
The phenylselenyl halides **29** can be generated *in situ* by the reaction of diphenyldiselenide and sulfurylchloride or bromine in acetonitrile. Treatment of disulphides (phenyldisulphide) with chloramine T affords a series of reagents which react with olefins to give adducts; the nature of these reactions is electrophilic, with $C_6H_5S^+$ initiating the reaction and a complex nitrogen anion terminating the process[90] (Scheme 17).



R = Ts = SO_2–$C_6H_4(CH_3)p$

Scheme 17.

At last is should be noted that allylic amination of olefins was performed using molybdo-oxaziridine complexes[91] as **31**.



(31)

(B) AMINO GROUP ACTIVATION

I. *Radical amination reactions*

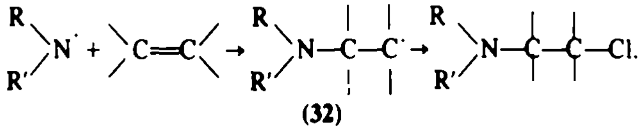
The chemistry of nitrogen radicals which are useful intermediates in organic synthesis has been discussed in several reviews.[92-96] Reactivity depends on their electrophilic character and therefore on electronic density of nitrogen in R–$\dot{N}$–X, this term being controlled by electron donating of withdrawing ability of group X, proton or transition metal M$^+$ binding to nitrogen.

Thus protonated aminoradicals RR'$\dot{N}$H, complexed amino radicals RR'N$^{\cdot}$ → $^+$M and some neutral aminoradicals R–$\dot{N}$–X bearing electron withdrawing groups X (R alkyl X: –C(=O)–Z with Z: alkyl or O–alkyl) behave as electrophilic species; they add efficiently to many types of unsaturated hydrocarbons in preference to abstraction of activated hydrogen as do other amino radicals (e.g. allylic abstraction as in following example[97]):

$$(CH_3)_2N^{\cdot} + C_6H_5C(CH_3){=}CH_2 \rightarrow (CH_3)_2NH + C_6H_5C(\dot{C}H_2){=}CH_2$$

$$(CH_3)_2N^{\cdot} + C_6H_5C(\dot{C}H_2){=}CH_2 \rightarrow C_6H_5{-}\underset{}{\overset{CH_2\\ \|}{C}}{-}CH_2{-}N(CH_3)_2.$$

These addition reactions to olefinic carbon–carbon double bond provide functionalized amines with specificity for the site of nitrogen atom binding; the amino group is always fixed on the least substituted carbon atom (anti-Markonikov):

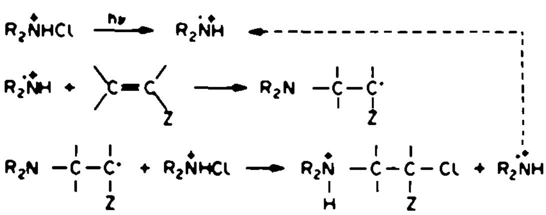


(32)

Other types of α-functionalized amine derivatives can be obtained according to this addition reaction pathway, depending on the stabilisation mode of the carbon radical **32**. Using different experimental conditions (e.g. chemical structure and decomposition way of precursors, solvent, absence or presence of oxygen, etc.) compounds such as amino-alcohols, ethylenic amines, or diamines are obtained with high specificity.

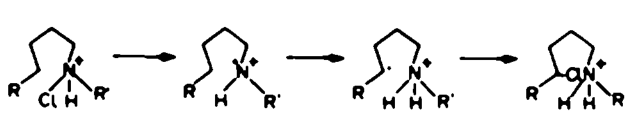
1. *Aminium radical additions*

Protonated amino radicals usually generated by photolytic or metal ion-catalyzed decomposition of N-chloramines in strong acidic media add to a variety of olefins. The reaction proceeds via a radical–chain sequence (Scheme 18).[98–101]

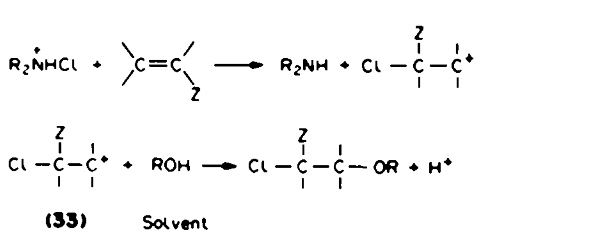


Scheme 18.

Most significant results are given in Table 10. The free radical amino–chlorination is effective with conjugated alkenes such as dienes with which the limiting competitive Hofmann–Loffller rearrangement does not occur. An example of this rearrangement (which occurs with long carbon chains) is given below:

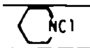
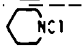
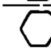
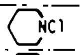
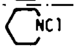
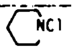
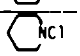
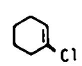
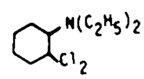
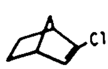


Moreover, yields are good with weakly deactivated alkenes such as $CH_2{=}CHCH_2X$ where X is an electron withdrawing group. In this case electrophilic chlorination by Cl^+ does not compete owing to the unstability of the resulting carbonium ion **33** (Scheme 19).



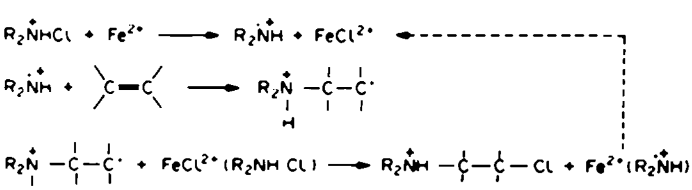
Scheme 19.

Table 10. Light-catalysed addition of chloramines to olefins in 4M sulfuric acid–acetic acid at 30°

Chloramine	Olefin	Adduct	Yield %
$(C_2H_5)_2NCl$	$CHCl{=}CHCH_3$	$(C_2H_5)_2NCH(CH_3)CHCl_2$	54
$(C_2H_5)_2NCl$	$CH_2{=}CHCl$	$(C_2H_5)_2NCH_2CHCl_2$	82
$(C_2H_5)_2NCl$	$CH_2{=}C(Cl)CH_3$	$(C_2H_5)_2NCH_2CCl_2CH_3$	84
$(C_2H_5)_2NCl$	$CH_2{=}CBrCH_3$	$(C_2H_5)_2NCH_2CBrClCH_3$	46
	$CH_2{=}C(Cl)CH_3$	 $NCH_2CCl_2CH_3$	92
	$CH_2{=}C(Cl)CH_2Cl$	 $NCH_2CCl_2CH_2Cl$	85
	$CH_2{=}C(CF_3)CH_3$	 $NCH_2CCl(CF_3)CH_3$	88
	$CH_2{=}CHBr$	 $NCH_2CHBrCl$	77
$(C_2H_5)_2NCl$	$CH_2{=}CHSi(CH_3)_3$	$(C_2H_5)_2NCH_2CHClSi(CH_3)_3$	65
$(C_2H_5)_2NCl$	$CH_2{=}C(CH_3)_2$	none	
$(C_2H_5)_2NCl$	Cis-$CH_3CH{=}CHCH_3$	none	
$(C_2H_5)_2NCl$	$CH_2{=}CHCH_2OH$	$(C_2H_5)_2NCH_2CHClCH_2OAc$	48
$(C_2H_5)_2NCl$	$CH_2{=}CHCH_2OC_6H_5$	$(C_2H_5)_2NCH_2CHClCH_2OC_6H_5$	6
	$CH_2{=}CHCH_2OC_2H_5$	 $NCH_2CHClCH_2OC_2H_5$	88
	$CH_2ClCH{=}CHCH_2Cl$	 $NCH(CH_2Cl)C(Cl)HCH_2Cl$	73
$(C_2H_5)_2NCl$			60
$(C_2H_5)_2NCl$		none	

Contrarily, with simple alkenes, electrophilic chlorination prevails (carbonium ion 33 is more easily formed than radical of aminochlorination). Also, radical amination fails with too strongly deactivated alkenes where electron depletion is too important.

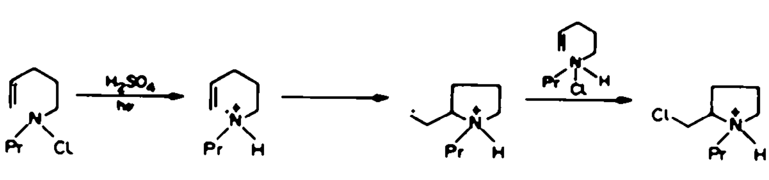
Minisci *et al.* developed an improved catalytic process (Scheme 20) in which electrophilic chlorination does not occur because the amino radical generated by ferrous ion catalysed decomposition of protonated N-chloramine adds faster to carbon–carbon double bond than does Cl^+. So with simple alkenes, the redox chain sequence operates effectively.[102]



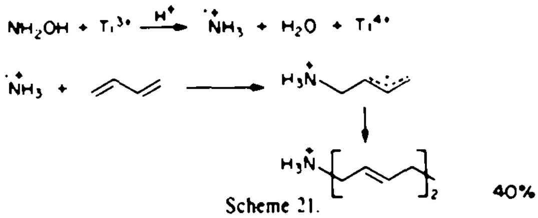
Scheme 20.

The synthetic utility of these two complementary methods should be emphasized since β-chloramines are not readily available by any other one step process involving unsaturated hydrocarbons.

Moreover reactions conducted with suitable ethylenic N-chloramine afford selectively five membered heterocycles[103–105] with fairly good yields; an example is given.[103]



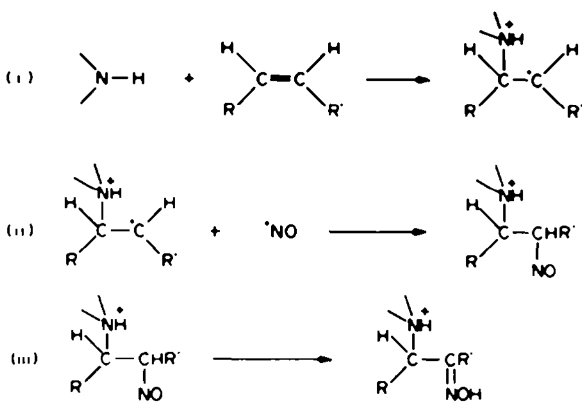
The aminium radical $\dot{N}H_3$ is produced when hydroxylamine is reduced by titanium(III) chloride in aqueous acidic methanol. In the presence of a diene or a simple alkene, addition occurs and is followed by dimerisation of the two resulting carbon radicals leading to ethylenic diamines[106-110] (Scheme 21).



Scheme 21.

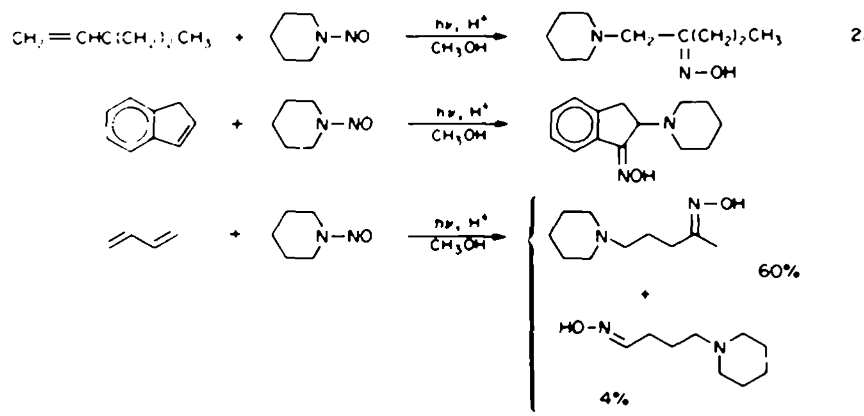
This process can be catalytic if titanium(III)-chloride is regenerated *in situ* by chemical or electrochemical reduction of the formed titanium(IV).[110]

However, hydroxylamine and N-haloamines are not exclusive precursors to aminium radicals. These ions can be also generated, as shown by flash excitation techniques[114] in dilute acids by aliphatic nitrosamine photolysis.[111-116] There, the mild conditions compared to N-chloramines decomposition make the process more versatile in synthesis. The proposed mechanism of this reaction, developed by Chow *et al.* is given below[115] (Scheme 22).



Scheme 22.

The resulting C-nitroso compounds can react in various thermal or photolytic secondary reactions. But if there is an α-hydrogen, irreversible tautomerization is the dominant process under photolysis conditions (Scheme 22; eqn (iii)). The efficiency of N-nitrosopiperidine photoaddition to various olefins decreases with olefin used in the following order $C_6H_5CH{=}CH_2$ > $RCH{=}CH_2$ > *cis*-RCH=CHR > $(CH_3)_2C{=}C(CH_3)_2$ > *trans*-RCH=CHR in which R is an alkyl group.[115] These photoaddition reactions are regiospecific; attack by aminium radicals always leads to the more stable radical intermediate. A conjugated diene such as 1,3 pentadiene being more reactive, adds with slightly less regiospecificity to give 1,4-adducts. Some examples[116] are presented in Scheme 23.



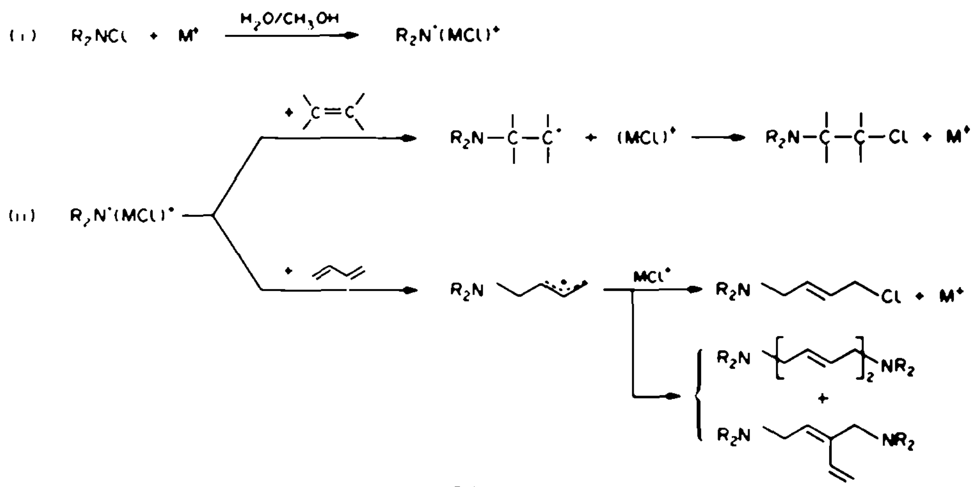
Scheme 23.

The electrophilic nature of the radical addition is demonstrated by competive photoaddition of N-nitrosopiperidine to substituted styrenes; addition is facilitated by electron-releasing substitutents with ρ value -1.29, implying an electrophilic character of the radical.[116]

According to Chow, other aminium radicals precursors can be used for hydrocarbon amination such as mono protonated tetrazene which are photolytically dissociated into two dimethylaminium radicals.[117]

2. *Complexed amino-radicals additions*

Aminoradicals produced from redox reactions of non-protonated N-chloramines[118] (and also hydroxylamine[119] or hydroxylamine-O-sulfonic acid[119]), with metal ion in aqueous methanol add to unsaturated hydrocarbons as follows (Scheme 24).[118-124]



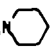
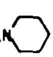
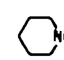
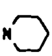
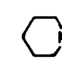
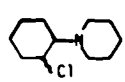
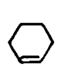
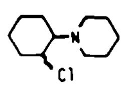
Scheme 24.

The amino radicals produced in this way, which are coordinated to the metal ion, exhibit the same electrophilic properties as aminium radicals generated in a strongly acidic system. The reactions of dienes with amino radicals formed with ferrous sulphate, and which cannot transfer chlorine atom, give mainly diamines whereas redox system such as $CuCl/CuCl_2$ promotes the aminochlorination route as shown in Table 11.[120,121] Appropriate conditions have been found (e.g. greater than catalytic amounts of metal salts) for aminochlorination of simple alkenes; some significant results are presented in Table 12.

Table 11. Addition of N-chloramine to butadiene in methanol solution induced by redox-system

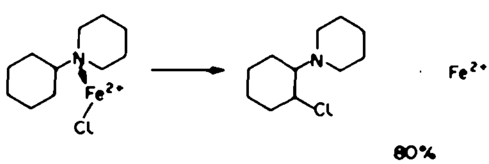
N-Chloramine	Redox-system	Adduct, yield % (based on N-Chloramine)	
		AminoChloruration	diamine
piperidine-NCl	$FeSO_4$	13.5	80
piperidine-NCl	CuCl $CuCl_2$	60	0
$(C_2H_5)_2NCl$	$FeSO_4$	5	64
$(C_2H_5)_2NCl$	$FeSO_4$ $CuCl_2$	54	0
$(CH_3(CH_2)_3)_2NCl$	$FeSO_4$ $FeCl_3$	30	48
$(CH_3(CH_2)_3)_2NCl$	CuCl $CuCl_2$	40	0

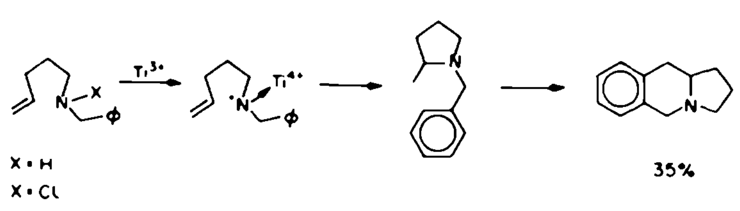
Table 12. Addition of N-chloramine to olefin in methanol solution induced by redox-system

N-Chloramine	Olefin	Redox-System	Adduct , Yield %
NCl	$C_6H_5CH{=}CH_2$	$FeSO_4$ $FeCl_3$	$C_6H_5CH(Cl)CH_2N$ 48
NCl	$p\text{-}ClC_6H_5CH{=}CH_2$	$FeSO_4$ $FeCl_3$	$p\text{-}ClC_6H_5CH(Cl)CH_2N$ 53
$(CH_3(CH_2)_3)_2NCl$	$CH_3(CH_2)_3CH{=}CH_2$	$FeSO_4$ $FeCl_3$	$CH_3(CH_2)_3CH(Cl)CH_2N((CH_2)_3CH_3)_2$ 43
NCl	$CH_3(CH_2)_3CH{=}CH_2$	$FeSO_4$ $FeCl_3$	$CH_3(CH_2)_3CH(Cl)CH_2N$ 65
NCl	$(CH_3)_2C{=}CHCH_3$	$FeSO_4$ $FeCl_3$	$(CH_3)_2C(Cl)CH(CH_3)N$ 61
NCl		$TiCl_3$	 69
NCl		$FeSO_4$ $FeCl_3$	 80

Moreover it is worthy of note that stereochemistry depends on reaction conditions; for instance unprotonated chloropiperidine adds to cyclohexene giving the *cis* isomer, whereas the corresponding protonated N-haloamines give rise to both *cis* and *trans* forms. The *cis*-stereoselectivity may be related to coordination of the unprotonated amino group with ferric salt which is mainly responsible of the chlorine atom transfer.[118,119,124]

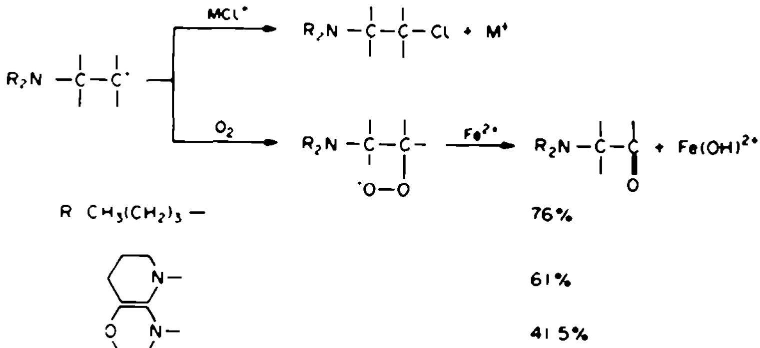
The reaction has been used in heterocyclic chemistry,[125,126] for example[126]



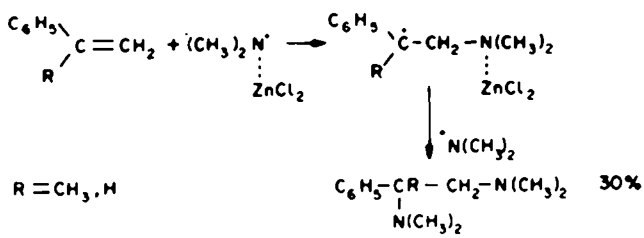


A new synthesis of α-aminoketones was developed by performing the addition reaction in the presence of oxygen.[127] The yields obtained with conjugated alkenes (e.g. styrene) are always high if based on the olefin but vary widely (41 to 76%) if based on the chloroamine. A plausible pathway is presented in Scheme 25.

Other complexed amino radicals precursors have also been developed for hydrocarbon amination. Michejda and Campbell reported that dimethyl amino radicals complexed by zinc chloride are generated by thermal decomposition (60°) of the tetramethyl-2-tetrazene:zinc chloride complex (TMT:$ZnCl_2$). In absence of oxygen they add to styrene, α- and β-methyl styrene and indene to give the corresponding bis (dimethyl amino) adducts.[128–131] Addition of the two dimethylamino groups is a stepwise process[130] (Scheme 26).



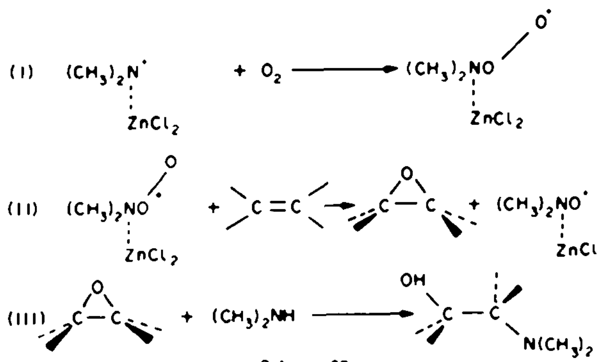
Scheme 25.



Scheme 26.

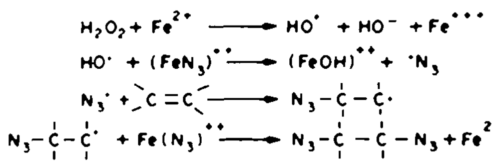
Relative rates of addition of the zinc chloride complexes amino radicals to substituted α-methyl styrene are well correlated by the Hammett equation with a ρ value -0.98 ± 0.04, whereas uncomplexed radicals give a ρ value $+0.69 \pm 0.03$.[129] These significant results support evidence of electrophilic character of complexed amino radicals in contrast to uncomplexed radicals.

When the reaction is performed in presence of oxygen, aminoalcohols are obtained with styrene and α-methylstyrene (30–40%)[131] probably by the same process mentioned in Scheme 25. But with compounds such as indene or *trans* β-methylstyrene some "abnormal" products are found. The authors assumed that they can be accounted for by reaction (iii) Scheme 27.[131]



Scheme 27.

Minisci *et al.* have obtained 1,2-diazides, which can be then transformed into 1,2-primary diamines, by radical addition of azide ion N_3^- to alkenes with good yields (e.g. styrene; 89%). The reaction is induced by an oxidant system, Fenton's reagent ($H_2O_2 + Fe^{2+}$) as shown below,[132] or $S_2O_8^{2-}$.

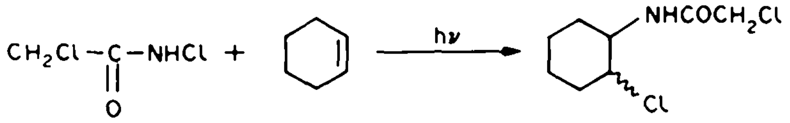


Scheme 28.

In presence of $FeCl_3$, azidochloruration occurs (e.g. with cyclohexene; yield 80%). Moreover, according to Schafer, similar di-azidation reaction can occur when the radical $N_3^{\cdot}$ is generated by electrochemical procedure.[135]

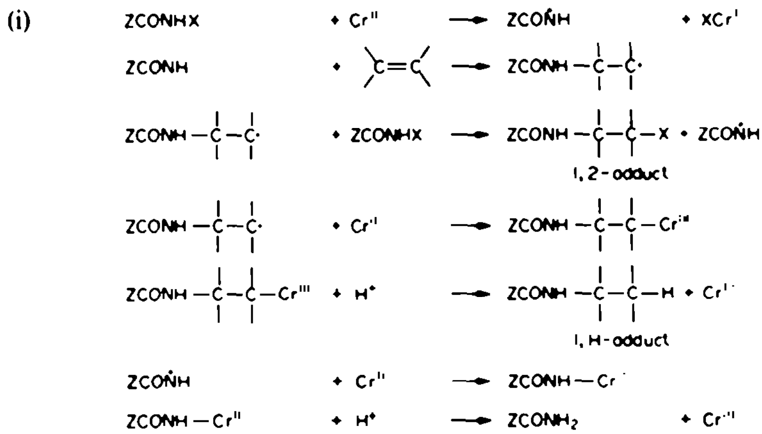
3. *Amidyl radical additions*

Acylamino radicals formed by photolysis of N-halocarboxamides RCONHX add to a variety of unsaturated hydrocarbons giving 1,2-addition products.[96,136,137] With use of α-halogenated substituted N-halocarboxamides, yields and amounts of *cis* isomer over *trans* are higher.[139] The efficiency of N-halocarboxamide photoaddition to alkenes is related to R as indicated by the sequence $CH_3 < CH_2Br < CH_2Cl = CH_2F < CHCl_2 < CCl_3$.[136]



91% (cis: 73%, trans: 18%)

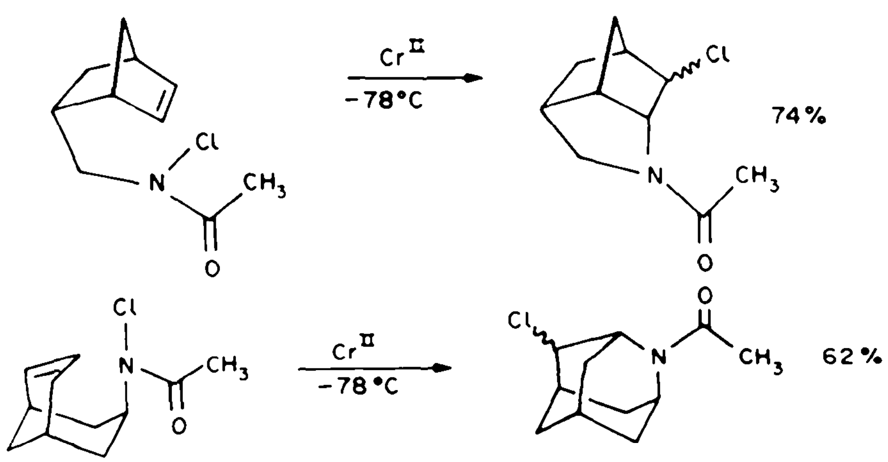
In these reactions the halogen atom X can compete with the amido radical. Thus the failure of certain N-halocarboxamides (e.g. N-bromo-) to add to unsaturated hydrocarbons might be explained by the greater reactivity of the halogen atom. So an improved process in which radical addition is unduced by chromous chloride was developed by Lessard *et al.* (Scheme 29).[138-140]



Scheme 29.

The amido radical is produced (eqn (i)) without concomitant formation of halogen atom which is trapped by the chromous salt; competitive halogenation cannot therefore occur.

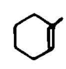
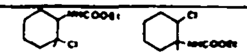
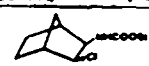
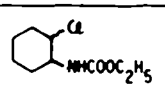
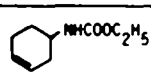
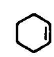
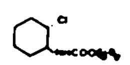
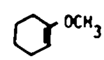
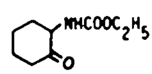
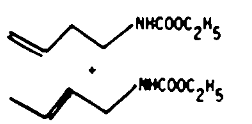
Furthermore this mild process has been largely developed in heterocyclic synthesis. For instance:[141]



Scheme 30.

Similar reactions of N-chlorinated urethanes (NCU) and N,N-dichlorourethanes (DCU) with alkenes have also large synthetic utility; 1,2-addition products are obtained with better yields than with the corresponding N-halocarboxamides. The DCU method complements that of N-chloramine additions as a

Table 13. Addition of N-chlorourethanes to olefins and conjugated dienes

N-Chlorourethane	Olefin or Diene	Initiator	Product (Yield%)	Ref.
$C_2H_5OCONHCl$	$C_6H_5CH{=}CH_2$	none	$C_6H_5CHClCH_2NHCOOC_2H_5$ 80	143
$C_2H_5OCONHCl$	$CH_3CH{=}CHCH_3$ (cis or trans)	hν	$CH_3CHCl(CH_3)NHCOOC_2H_5$ 94	144
$C_2H_5OCONHCl$	$CH_3(CH_2)_5CH{=}CH_2$	$CrCl_2$	$CH_3(CH_2)_5CHClCH_2NHCOOC_2H_5$ 85	142
$C_2H_5OCONHCl$		$CrCl_2$	 trans 3% trans 1,6% cis 77% cis 5,4%	142
$C_2H_5OCONHCl$		$CrCl_2$	 Cis 35% trans 6%	142
$C_2H_5OCONHCl$		$CrCl_2$	 87	138
$C_2H_5OCONHCl$		$CrCl_2$	 78	138
$C_2H_5OCONCl_2$		none	 30	143
$C_2H_5OCONHCl$		$CrCl_2$	 85	138
$C_2H_5OCONHCl$		$CrCl_2$	 37 + 37	138

route to N-protected β-chloroalkylamines with the nitrogen atom fixed on the less substituted alkene carbon atom. Moreover, this method also affords adducts with electron-poor alkenes such as acrylate monomers. Most significant results are given in Table 13.

Both N-chloro and N,N-dichloroalkanesulfonamides add to various olefins and dienes.[145-148] The monochlorosulfonamide reactions are clean but require photolytic initiation, whereas dichlorsulfonamide reactions are spontaneous but more complex.

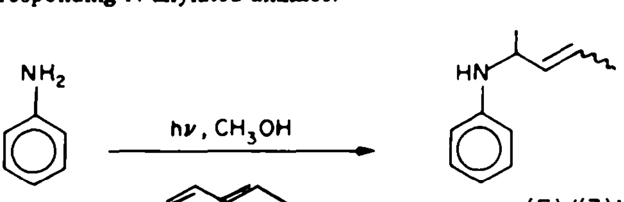
Photolysis induced reactions for the latter are more regioselective affording only anti-Markovnikov 1,2-adduct:

$$RSO_2-NCl_2+CH_2=CHR' \xrightarrow[N_2,\,CH_2Cl_2]{h\nu} RSO_2-\underset{\displaystyle Cl}{\underset{|}{N}}-CH_2-\underset{\displaystyle Cl}{\underset{|}{N}}-CHR'$$

$R=C_6H_5$ R′: CH_3 53%

4. *Photochemical amination reactions*

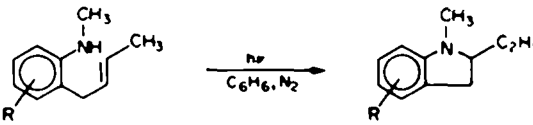
When irradiated in solution, aromatic amines in presence of excess 1,3-diene (e.g. butadiene, isoprene) yield corresponding N-allylated anilines.[149]



(E)/(Z): 16,6 %

Structures of compounds produced can be accounted for by formation of an electron-donor-acceptor complex of the aniline and the diene in the singlet state followed by intramolecular proton transfer from N-H group to the 1,3-dienyl radical anion.

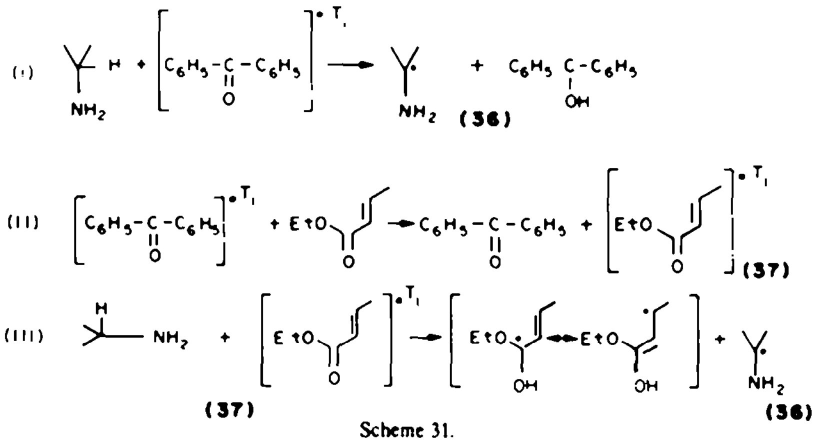
Photochemical amination has also been used to promote intramolecular amination of carbon-carbon double bond; for instance, photocyclization of allylanilines 34 leads to indolines[150] whereas irradiation of N-allylimminium salts 35 gives pyrrolidines[151] (Scheme 30).



(34)

(35)

Also photochemical addition of alkylamines[155-158] or formamide $HCONH_2$[152-154] to alkene occurs. These can be very selective toward 1,2-adduct formation if performed in the presence of photosensitisers such as acetone[153,154] or benzophenone respectively. It has been assumed that these compounds do not react like classical photosensitisers; rather, acetone or benzophenone in their excited state can abstract hydrogen from formamide or amine in their ground state (eqn (i); Scheme 31) leading to radicals 36 which further add to olefin. With activated olefin such as ethylcrotonate 37, the mechanism is more complex.[155] Indeed the active radical 36 may be produced by reaction of alkene triplet excited state 37 with amine (eqn (ii) and (iii); Scheme 31).



Scheme 31.

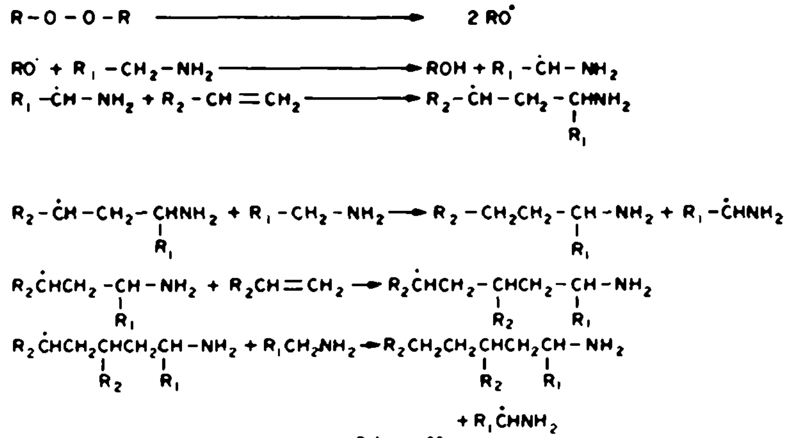
Similar studies using γ-ray or electron beam[159-162] have been reported.

5. *Peroxide promoted radical additions*

When induced by a peroxide, amination reactions are not so selective towards 1,2-adduct formation; the active radical formed, centred on a carbon atom, gives rise to the classical chain radical reactions presented in Scheme 32.

II. *Alkaline metal catalysed reactions*

The direct addition of ammonia and amines to alkenes is a potentially useful synthetic reaction. Whereas general conditions have not yet been established, the addition is efficient when formation of the amide anion is facilitated (high temperature, use of an alkaline metal such as Na, Li).[165] Thus reactions conducted with monoalkenes[166-168] require drastic conditions (high temperature and pressure) and produce N-alkylated amines. Mixtures of tri-, di-, and monoalkylated compounds are formed depending upon the nature of the amine; also, by-products such as polymers are formed. However the same



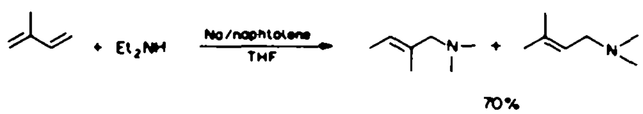
Scheme 32.

reactions using conjugated dienes or styrene proceed more easily and have found wide application in β-γ unsaturated amines synthesis.[169,170]

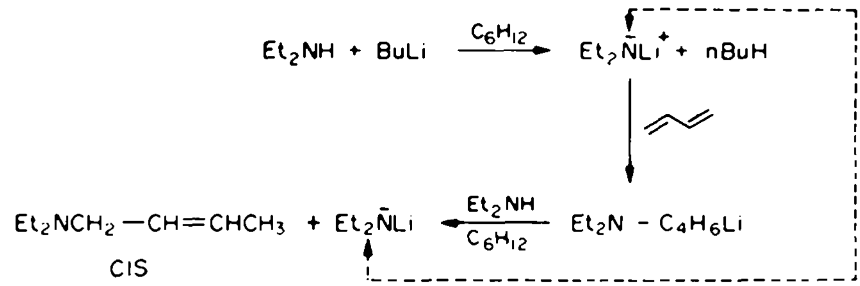
$$CH_3CH{=}CH{-}CH{=}CH_2 + (CH_3)_2NH \xrightarrow[Et_2O]{Na} CH_3CH_2CH{=}CH{-}\underset{\displaystyle CH_3}{\underset{|}{C}H}{-}N(CH_3)_2$$

50 to 80%.

Under similar conditions and in presence of naphthalene, the reactive amide ion is likely formed by the attack of amine (weak acid) on the radical anion obtained from the sodium/naphthalene reagent. Following this route, conjugated dienes afford mixture of β-γ unsaturated amines in good yields.[171]

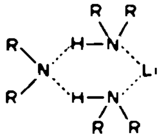


Among studies of the application of this process in synthesis, an interesting result was obtained by Narita *et al.* who found that diethylamine can add stereospecifically to butadiene if three equivalents of amine are used for one of butyl-lithium. The adduct formed is only *cis*-1-dimethylamino-2-butene.[172-174]



Scheme 33.

It has been proved by kinetic and spectroscopic experiments (IR and NMR) that an intermediate such as **38** must be involved.[173] Moreover the large ρ value ($+5$) obtained with substituted styrenes support evidence of the strong nucleophilic character of these addition reactions.[174]

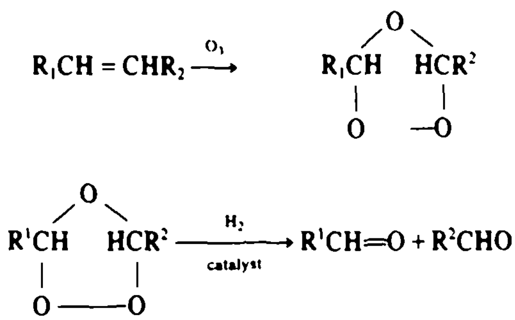


(38)

(C) MISCELLANEOUS

White *et al.*[175] used the well-known addition reaction of amines to carbonyl compounds to develop a "one pot" synthesis of alkylamines from alkenes and amines; the carbonyl compound is obtained by ozonolysis of the carbon–carbon double bond. The reaction proceeds via three distinct steps as indicated in the following scheme:

(a) ozonolysis of the alkene:



(b) reductive amination

$$R^1CH{=}O + O{=}CHR^2 \xrightarrow[R'R''NH]{H_2,\ catalyst} R^1CH_2NR'R'' + R^2CH_2NR'R''$$

R_1: $CH_3(CH_2)_{13}$–; R_2: H; R′=R″=CH_3 yield: 65%

α-olefins give with fair to good yields alkylamines bearing one carbon atom less than the starting olefin.

Along the same lines, one should mention the catalytic process developed by Kraiman;[176] amines with nitrogen atom added to the terminal carbon atom of the starting 1-alkenes are synthesised according to a combination of classical reactions:

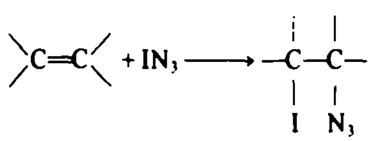
$$HBr + RCH{=}CH_2 \xrightarrow{catalyst} RCH_2CH_2Br$$

$$\downarrow + (CH_3)_2NH$$

$$HBr + RCH_2CH_2N(CH_3)_2.$$

Diborane adds to carbon–carbon double bonds to yield alkylboranes R_3B which are then treated by an aminating reagent, such as an N-chloroamine, to give amines. This hydroboration–amination process developed by Brown gives products corresponding to an anti-Markovnikov addition of amine to the alkene;[177-180] it follows the same mechanism as that described for hydroboration–oxidation of alkenes.[181] Some significant results are given in Table 14.

According to Hassner *et al.*[182,183] the addition of iodine azide, generated *in situ*, to alkenes leads to β-iodo alkyl azides **39** in good yield.

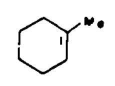
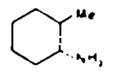
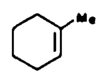
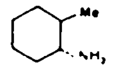
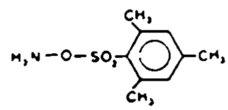
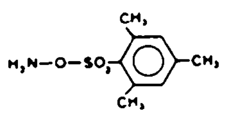
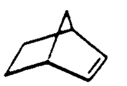
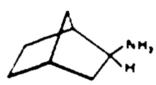
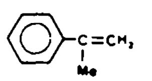
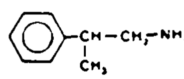
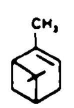
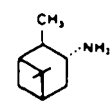


(39)

cyclohexene	82%
styrene	70%
cis-2-butene	67% (threo-)

Compound **39** can be further reduced with diborane to give the corresponding α-amino–β-iodoalkane. This addition occurs in a *trans* fashion. Data obtained with various alkenes are rationalized by assuming the formation of an iodonium ion intermediate (an alkene activated by iodide ion) which is further opened in a *trans* diaxial process.[182]

Table 14. Hydroboration–amination of alkenes

amination reagent	Olefin	Adduct Yield(%)	Ref.
NH_2-OSO_3H		 trans 58	180
NH_2Cl		 trans 5,5	177
	$CH_3(CH_2)_7CH=CH_2$	$CH_3(CH_2)_8CH_2$-NH_2 24	179
		 exo 49	179
NH_2Cl or NH_2-OSO_3H		 58	177
NH_2-OSO_3H		 58	180

This reaction was then extended to various unsaturated hydrocarbons (e.g. 1-acylindoles,[184] strained cyclobutenes,[185] *trans*-cyclooctene[186]).

When bromine azide is used instead of iodine azide for the similar addition, a competitive free-radical pathway interferes.[187,188]

Heterogeneous catalytic methods directed to amination of olefins have undergone considerable industrial development as indicated by the extensive patent literature. These reactions are run under drastic conditions (high pressure and temperature) leading to mixtures of corresponding amines and nitriles; therefore they seem to be excluded from laboratory synthetic use.[189]

CONCLUSION

In summary, organic chemists have made available different synthetic reactions for the functionalization of an unsaturated carbon chain, to give an amine, an aminoalcohol, a diamine, or a haloamine.

The ionic route (through metal activation of the double bond) provides regiospecific and in some cases stereospecific simple processes; palladium and mercury have been more commonly used, the drawback of the method being the requirement of a carbon–metal cleavage step and metal recycling. However, this second step can be used for introducing a second functional group. More recent developments with osmium and selenium (with the possibility for the former of using catalytic amounts) seem promising.

Aminyl and amidyl additions to alkenes offer an interesting complementary route; understanding of these reaction mechanisms has led to defined experimental conditions giving good yields of amines and functionalized compounds such as protected haloamines, in regio- and stereoselective procedures.

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