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Amines acting as hydride ion donors in reactions with unsaturated electrophilic compounds

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ABSTRACT. The reactions involving reduction of electrophilic double bonds (C=C, C=O, C=N, and N=N) with amines (usually tertiary) that contain hydrogen atoms at the α-position have been classified. The key stage in such reactions is formation of an iminium salt, which can formally be regarded as the transfer of a hydride ion from the amine to the compound with a double bond, although the actual mechanism may be different. The subsequent reactions of the intermediates formed (iminium cations, enamines, aminocarbenes), including acylation and cycloaddition, are examined. The synthetic potentialities of these reactions for obtaining different functionally substituted linear and heterocyclic compounds are discussed.

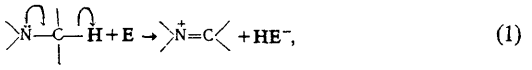
The bibliography includes 127 references.

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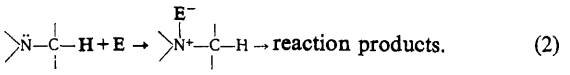
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I. Introduction

Aliphatic, alicyclic, and heterocyclic amines that contain hydrogen atoms at the α-position are potential donors of hydride ions and can participate in the reduction of sufficiently active electrophilic compounds [equation (1)]. This ability to eliminate a hydride ion and form an iminium cation is in many cases suppressed by competing reactions which start with addition of the electrophilic partner [equation (2)].[1]

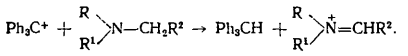


(1)



(2)

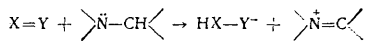
Nevertheless, oxidation reactions of hydrocarbon residues in amines occur quite widely and can be effected by treatment with stronger or weaker oxidising agents such as free halogens,[2,3] other inorganic oxidising agents,[4] and also classical hydride ion acceptors[5,6] such as triarylcarbenium ions:1,7–12



A reaction of the latter type is responsible for the thermal decolorisation of triarylmethane dyes containing a carbocation site together with dialkylamino groups.[13]

The electrochemical oxidation of amines is also well known.[14] Their fermentative oxidation is of considerable significance in nature.[4]

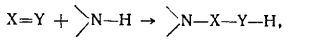
Among those reagents capable of reactions which may formally be regarded as the elimination of a hydride ion from the α-position of the amine are various unsaturated electrophilic compounds containing double bonds—activated olefins, carbonyl compounds, their hetero analogues, etc. Quite a considerable amount of material on reactions of this type [equation (3)] has been collected to date.



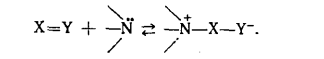
(3)

An attempt has been made in this review to classify this material, with thermal reactions mainly being studied. The electrochemical[14] and photochemical[15] oxidation of amines have been the subjects of extensive reviews.

Tertiary amines are usually involved in reactions of type (3), secondary or primary amines are involved less frequently. This is probably because in the latter cases there is the possibility of other reactions, mainly addition to the double bond [equation (4)]. Tertiary amines can also add on to double bonds such as C=C[16–19] or C=O[20–22] but as a rule these reactions are reversible [equation (5)].



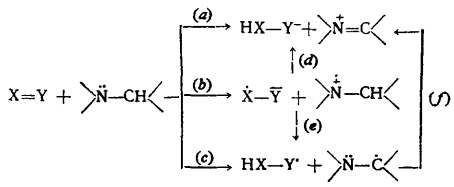
(4)



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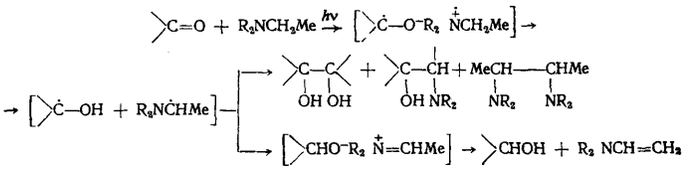
In principle reactions of type (3) can occur by at least four routes (Scheme 1): 1) direct hydride transfer (*a*); 2) transfer of e^- to form a radical ion pair [usually via a charge-transfer complex (CTC)], then transfer of H^+ and transfer of e^- again (*b*)–(*e*)–(*f*); 3) transfer of e^-, then transfer of $H^\cdot$ (*b*)–(*d*); 4) transfer of $H^\cdot$ followed by transfer of e^- (*c*)–(*f*).

Scheme 1



Sometimes the direct transfer of a hydride ion [variant (1)] is assumed for these types of reactions, but mechanisms involving the formation of an intermediate CTC [variants (2) and (3)] would usually appear to be more likely.[4,23–27] Evidence in favour of these is the frequently observed instant colour change when the reactants are mixed and the frequent cases of complexes of amines with different electron acceptors being formed, unaccompanied by further reactions.[23–25,28,29]

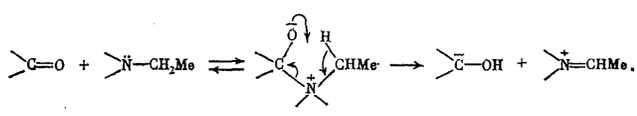
Variant (2) usually occurs in the photochemical oxidation of amines.[15,30–33] Free radicals formed at stage (*e*) can both disproportionate to an anion and cation [stage (*f*) and also couple,[15,30–32,34–37] for example:



In addition, these free radicals can be identified using t-nitrosobutane as a "trap".[38] It cannot be excluded that in certain photochemical reactions a radical pair is formed directly from the reactants by H· transfer [variant (4)] and avoiding the radical ion stage.[32,39,40] There is evidence that the mechanism depends on the nature of the solvent; in nonpolar media a radical pair is formed directly while in polar media the reaction occurs via radical ions.[39,40]

Variant (3) usually occurs in thermal reactions and formation of free radicals is not observed†[23] (compare, however, the results of Ohno et al.[43]). The overall trend is that in photochemical reactions mainly free-radical coupling products are formed (for example, pinacones from carbonyl compounds[15,30–32]), while in thermal reactions products derived from the reaction of iminium salts are formed.

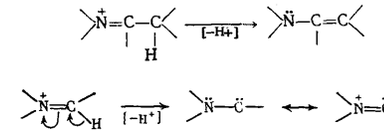
One further possible scheme for the oxidation of an amine by an unsaturated compound is fragmentation of the intermediate betaine with an "unconventional" transfer of the electron pair on cleavage of the C–N bond,[44–46] for example:‡



But however the reaction might occur—via a CTC, via a betaine, or as a result of direct hydride ion transfer—the oxidation of the amine leads to an iminium salt. In the majority of cases the actual mechanism has not been investigated; nevertheless, taking the result of the reaction as a basis, this type of conversion is usually called a hydride transfer.

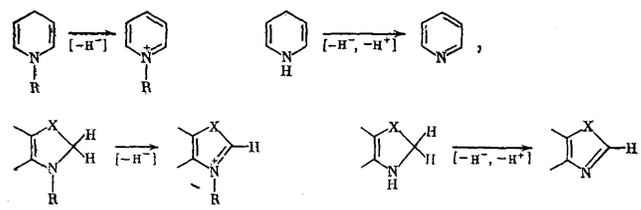
In some cases the iminium salt is the final product, in other cases it is an intermediate (identified by NMR, for example, or only postulated).

The anion component of the iminium salt HX–Y⁻ (⁻CHO⁻, ⁻CHN̄–, etc.) can add on a proton from the medium or deprotonate the iminium cation. An enamine is formed as a result of elimination of a proton from the β-position. When there are no hydrogen atoms at this position, an aminocarbene can be formed by α-elimination:



These reactive species are usually not isolated but undergo further reactions, for example, those involving a further molecule of the initial unsaturated compound.

Some of the most effective donors of hydride ions are dihydroaromatic heterocycles such as 1,4-dihydropyridines,§ thiazolines, and imidazolines. Thus, they can reduce hexafluoroacetone,[49,50] hexachloroacetone,[28,51,52] thiobenzophenone,[53] trifluoroacetophenone,[26,27] imines and enamines,[54] unsaturated carbonyl compounds,[55–57] haloquinones,[23] and carboxylic acid chlorides.[58] The driving force of these reactions is formation of an aromatic system:



However, sufficiently electrophilic double bonds can also be reduced by normal aliphatic, aliphatic-aromatic, or saturated heterocyclic amines.

It should be emphasised that the redox conversions that occur when amines react with unsaturated compounds are important from different viewpoints. Thus they can be used to synthesise from simple and accessible reactants, compounds which are difficult to obtain by another route. Typical examples are the syntheses based on triethylamine via an unstable intermediate diethylvinylamine (see below). Moreover, it is necessary to take into account the limitations that are imposed by the possibility of side reactions with the traditional use of tertiary amines as basic (or nucleophilic) reactants or catalysts.

II. Reduction of a C=C bond

For an olefinic double bond to have sufficient electrophilic reactivity, it must be activated with electron-withdrawing substituents. This condition is also necessary in the case of reactions with amine hydride ion donors.

1. Fluoroolefins

Fluoroolefins are fairly active in reactions with nucleophiles. However, tetrafluoroethylene does not react under normal conditions with tertiary amines. Some tertiary amines have been used as

† The acidity of radical cations of tertiary amines is low ($pK_a \sim 15$). This fact, together with the substantial decrease in strength of the α-C–H bond on going from an amine to its radical cation, is evidence in favour of variant (3) involving H· transfer.[41] For the different routes of radical cation fragmentation see Todres.[42]

‡ A "conventional" route is taken to mean the transfer of the bonding electron pair to the positively charged nitrogen atom, leading to decomposition of the betaine to the initial components.

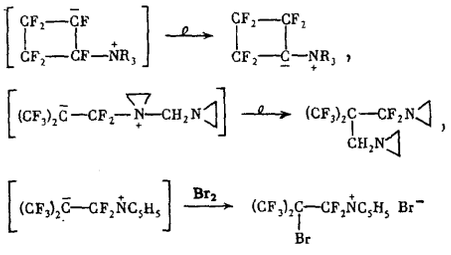
§ Coenzymes of the type NADH, which contain a dihydropyridine ring, play a most important part in biochemical oxidation-reduction processes.[47,48]

stabilisers to prevent spontaneous polymerisation of tetrafluoroethylene.[59] The reaction of tetrafluoroethylene with triethylamine on exposure to γ-radiation leads only to telomerisation products $Et_2NCHMe(CF_2CF_2)_nH$.[60]

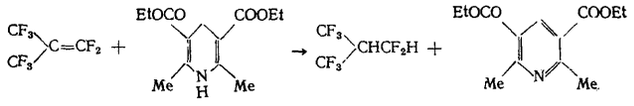
The more electrophilic perfluorocyclobutene and perfluoroisobutylene when reacted with tertiary amines evidently give bipolar ions, for example:

$$(CF_3)_2C{=}CF_2 + NR_3 \rightleftarrows (CF_3)_2\bar{C}{-}CF_2\overset{+}{N}R_3.$$

Indirect confirmation of this type of reaction is that the capacity of tertiary amines to catalyse the dimerisation of bis(trifluoromethyl)ketenimines is suppressed by the addition of perfluoroisobutylene (the rate of reaction is reduced by a factor of over 100).[16] In certain cases products derived by reaction of bipolar intermediates, being formed by rearrangements[16,17,61] or by reaction with an "external" electrophile,[62] have been isolated.



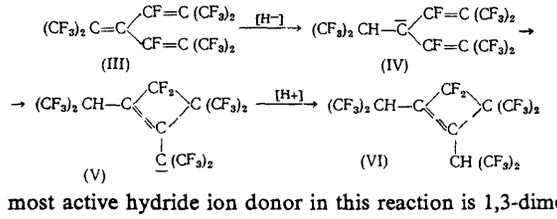
The tendency to form bipolar ions in which the hydride activity of hydrogen atoms is low may possibly also account for the fact that perfluoroisobutylene is not reduced by aliphatic or aliphatic-aromatic tertiary amines and only with Hantzsch ester does it give small quantities of dihydride at 120 °C.[63]



Perfluoroisobutylene reacts as a dehydrofluorinating agent with α,α-difluorotrimethylamine, converting it to the aminocarbene (I); the latter, on reacting with a further molecule of perfluoroisobutylene, is inserted into a C–F bond and gives amine (II):[64]

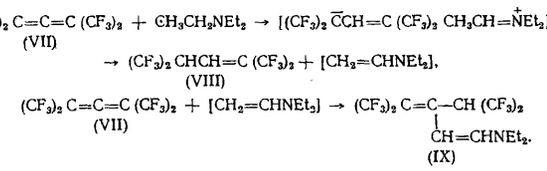
$$HCF_2NMe_2 \xrightarrow[-(CF_3)_3CH]{(CF_3)_2C=CF_2} [\ddot{C}FNMe_2] \xrightarrow{(CF_3)_2C=CF_2} (CF_3)_2C{=}CFCF_2NMe_2$$
(I) (II)

Introduction of two bulky perfluoroisobutenyl groups into the perfluoroisobutylene molecule inhibits the formation of a bipolar ion with a tertiary amine, at the same time not reducing the electrophilicity of the fluoroolefin. Therefore, the cross-conjugated perfluorotriene (III) readily removes a hydride ion from tertiary amines even at room temperature to form carbanion (IV). This linear carbanion then isomerises to the cyclic carbanion (V), and protonation of the latter gives the substituted cyclobutene (VI):[65]



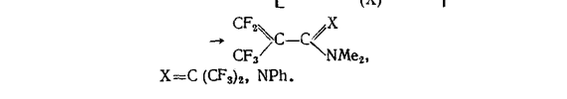
The most active hydride ion donor in this reaction is 1,3-dimethylbenzimidazoline; benzyldimethylamine and triethylamine have comparable activity.

Tertiary amines also reduce the cumulated C=C bond in tetrakis(trifluoromethyl)allene (VII).[66] Reaction with triethylamine at 65 °C results in the formation of the dihydroolefin (VIII) and dienamine (IX). The latter is evidently a product from the condensation of the initial allene (VII) and the intermediate diethylvinylamine:



With 1,3-dimethylbenzimidazoline, allene (VII) gives dihydroolefin (VIII) even at room temperature. Triphenylmethane and phenylacetylene have been used as proton donors in this reaction.[50]

Bis(dimethylamino)methane must have a greater hydride activity than triethylamine. However, when it is reacted with tetrakis(trifluoromethyl)allene or *N*-phenyl-bis(trifluoromethyl)ketenimine, reduction does not occur and there is an "allylic" substitution of a fluorine atom by a dimethylamino group [probably with formation of the intermediate betaine (X)], and the cumulated system of double bonds is converted to a 1,3-diene (or heterodiene) system:[67]

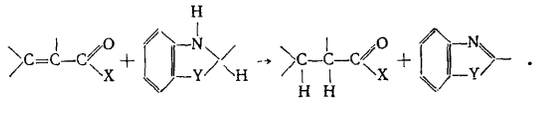


This type of cleavage on treatment with electrophilic reagents to form a dimethylaminomethyl cation which bonds with the anionic part of the electrophile is generally typical for bis(dimethylamino)methane.[68,69]

Thus, out of the fluoroolefins and related compounds studied only perfluorotriene (III) and allene (VII) undergo nucleophilic ionic hydrogenation (compare the results of three studies[6,50,65]) when treated with tertiary aliphatic and aliphatic-aromatic amines.

2. α,β-Unsaturated carbonyl compounds and their analogues

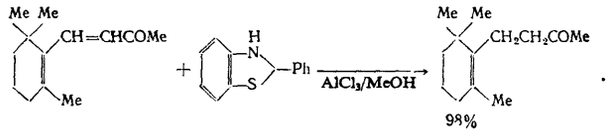
By using nitrogen-containing dihydroheteroaromatic compounds as reducing agents it has been possible in recent years to develop preparative methods for the hydrogenation of the C=C bond without affecting functional groups:



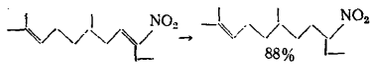
The reduction of a large number of activated olefins $RR^1C{=}CXY$ showed that the ease of reduction of the C=C bond decreases in the series of X, Y: CN, CN > CN, COOR > NO_2, H > COOR, COOR.[57] Replacement of R and R^1 by cyano groups increases the activity of the olefin even further, so that tetracyanoethylene is reduced not only by dihydroheteroaromatic but also by dihydroaromatic compounds such as 1,2-dihydronaphthalene.[70,71]

α,β-Unsaturated carboxylate esters and α,β-unsaturated ketones are reduced by dihydroheteroaromatic compounds only in the presence of Lewis acids.[56] In conjugated dienones it is possible to

reduce selectively just the α,β-C=C bond:[55]



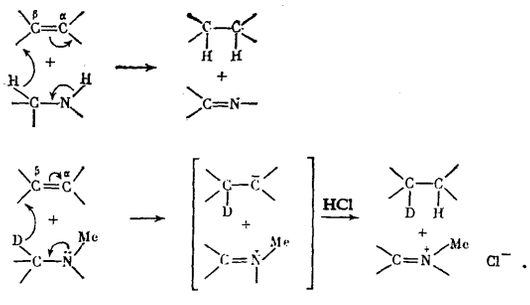
α,β-Unsaturated nitrocompounds and ketones are reduced with Hantzsch ester or 2-phenylbenzimidazoline in the presence of silica gel,[72–74] for example:



The increased hydride activity in 2-phenylbenzthiazolines from the introduction of electron-donating substituents into the *para*-position of the phenyl ring increases the rate of hydrogenation. This indicates that transfer of a hydride ion is the rate-determining stage of the reaction.[55] The use of benzthiazolines and benzimidazolines that were deuterated at the 2- and 3-positions showed that a hydrogen atom was transferred from the 2-position to the β-position and the hydrogen atom at the 3-position was transferred to the α-position of the compound undergoing hydrogenation.[55,57] In the reduction with 1,3-dimethyl-2-phenylbenzimidazoline, the hydrogen atom at the α-position relative to the functional group of the compound being reduced is derived from the solvent.[56]

In the reaction of (*Z*)-1,2-dibenzoyl-1,2-diphenylethylene with 2-phenylbenzthiazoline only *meso*-1,2-dibenzoyl-1,2-diphenylethane is formed stereospecifically. *cis*-Hydrogenation also takes place in the reduction of ethyl phenylpropiolate.[55]

When these results are combined it can be seen that in hydrogenation with benzthiazolines and benzimidazolines that have an unsubstituted nitrogen atom, transfer of the two hydrogen atoms to the C=C bond being reduced takes place simultaneously or almost simultaneously, while in hydrogenation with 1,3-dimethyl-2-benzimidazoline transfer of a hydride ion occurs [or correspondingly an electron and then a hydrogen atom (see Scheme 1)] followed by addition of a proton from the medium:[55–57]



Cyclic α,β-unsaturated carbonyl compounds such as halogenated quinones are some of the strongest electron acceptors. Their reactions with tertiary amines are examined in Section III.

If the C=C bond in the unsaturated compound is activated only by aryl substituents, this is insufficient for nucleophilic ionic hydrogenation by amines. Olefins such as styrene and stilbene react with tertiary amines only on irradiation, forming products from addition, hydrogenation, hydrodimerisation, etc.[36,39,40,75,76]

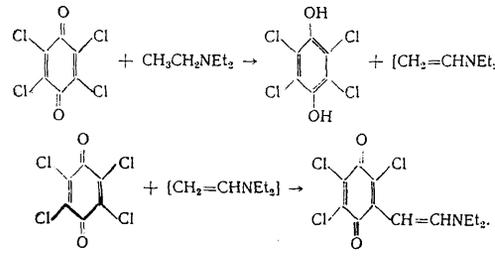
III. Reduction of a C=O bond

Although carbonyl compounds exhibit more marked electrophilic properties than do olefins, in the absence of electron-withdrawing substituents their activity is usually still insufficient for reduction by amines. Only on irradiation are benzophenone, acetophenone, and similar compounds reduced by amines since electron-transfer reactions are typical for the photochemically excited carbonyl group.[15] However, the presence of strong electron-withdrawing substituents in a carbonyl compound enables a hydride ion to be transferred to the unexcited C=O group. In this case reduction via decomposition of a betaine cannot be excluded (see Section I).

1. Haloquinones

Chloranil forms a CTC with tetramethyl-*p*-phenylenediamine[23] or 1,4-diazabicyclo[2.2.2]octane[29] and partially or completely (in polar solvents) isolated radical ion pairs.

When chloranil reacts with triethylamine, it is reduced to tetrachlorohydroquinone, and the resulting diethylvinylamine reacts with a further molecule of choranil, giving a compound with a blue colour—*N*, *N*-diethylaminovinyltrichlorobenzoquinone:[23,77]

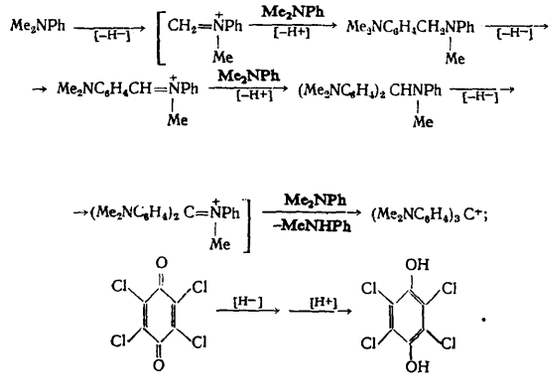


Other chlorinated quinones and also bromanil react in a similar manner to chloranil; iodanil does not react with triethylamine.[77,78]

Diethylcyclohexylamine, *N*-ethylpiperidine, diethylaniline, tetramethylethylenediamine, tribenzylamine, benzyldimethylamine, trimethylamine, tributylamine, and dimethylisobutylamine also have reducing properties in relation to chloranil. In the latter case the resulting enamine $Me_2C=CHNMe_2$ has been determined as isobutanal 2,4-dinitrophenylhydrazone.[77]

Replacement of the chlorine atoms in chloranil by methoxy groups leads to a weakening in oxidising properties; dichlorodimethoxybenzoquinones do not oxidise tertiary amines.

The formation of Crystal Violet when dimethylaniline is treated with chloranil under mild conditions may be due to the successive alternation of a hydride ion transfer to chloranil and electrophilic attack by the intermediate iminium cation at the *para*-position of a dimethylaniline molecule:[23]



2. Aldehydes and ketones

Hexafluoroacetone, which is a strong electrophile,[79] forms a stable iminium salt (XI)[49] with benzyldimethylamine. On hydrolysis of the salt, hexafluoroisopropanol and *N, N'*-dibenzyl-*N, N'*-dimethyldiaminomethane—a product of the condensation of methylbenzylamine with formaldehyde—are isolated. The hydride ion is mainly removed from a methyl group rather than the methylene group, which Gambaryan and Knunyants[49] attribute to steric hindrance:

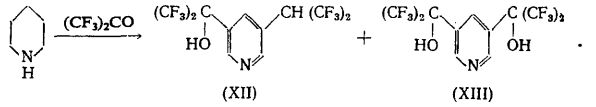
$$(CF_3)_2C{=}O + Me_2NCH_2Ph \rightarrow (CF_3)_2CHO\ CH_2{=}\overset{+}{N}CH_2Ph \xrightarrow{H_2O}$$
$$\underset{Me}{|}$$
$$\text{(XI)}$$
$$\rightarrow (CF_3)_2CHOH + PhCH_2NCH_2\underset{Me}{\overset{|}{N}}CH_2Ph\,.$$
$$\underset{Me}{|}$$

Hexafluoroacetone is also reduced to hexafluoroisopropanol when treated with triethylamine,[49] dimethylisopropylamine,[49] and dicyclohexylethylamine[80] (the fate of the respective iminium cations has not been studied). Benzyldiethylamine and tribenzylamine do not react with hexafluoroacetone even on heating to above 100 °C,[49] while a stronger acceptor—the triphenylcarbenium cation—can remove a hydride ion from tribenzylamine.[8]

Benzylamine reacts with hexafluoroacetone to give the adduct $(CF_3)_2C(OH)NHCH_2Ph$; heating the adduct to 160 °C followed by hydrolysis yields hexafluoroisopropanol.[49,81]

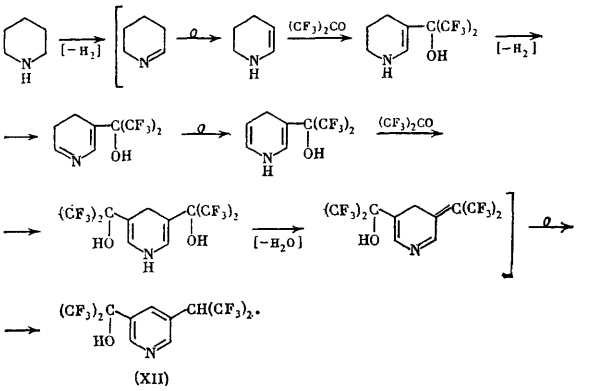
The $(CF_3)_2CHO^-$ anion has been detected by ^1H NMR spectroscopy in mixtures of hexafluoroacetone and trimethylamine, triethylamine, or diethylmethylamine. When there is excess hexafluoroacetone, there is a signal from the $(CF_3)_2CHOC(CF_3)_2O^-$ anion. Both anions have been isolated as *O*-trimethylsilyl derivatives on addition of trimethylchlorosilane.[82]

Hexafluoroacetone can also oxidise indoline, piperidine, and tetrahydroquinoline systems¶.[83–86] Thus, in the reaction of piperidine with excess hexafluoroacetone, substituted pyridines (XII) and (XIII) are formed:[83,85]



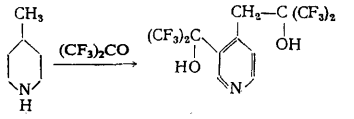
(XII) (XIII)

In this case aromatisation evidently results from a complex succession of reactions, involving not only the oxidation of amines by hexafluoroacetone but also the hydroxyalkylation of enamines, isomerisation of the intermediates with a double bond displacement, and also the dehydration of hydroxyalkyl-substituted enamines, for example:



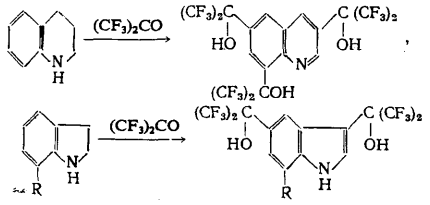
(XII)

In the case of α- and γ-pipecolines and also 2,6-dimethylpiperidine, hydroxyalkylation of both the heterocyclic ring and the methyl group occurs in addition to oxidation:[85]



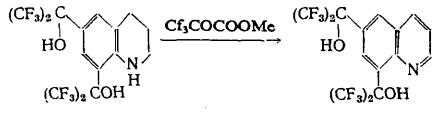
β-Pipecoline is substituted only in the ring.

In condensed systems such as tetrahydroquinoline and indolines, both rings can undergo hydroxyalkylation:[84,86]



It has been shown that in the reactions of piperidines and tetrahydroquinolines substitution takes place until the system is aromatised, as the corresponding aromatic heterocycles do not react with hexafluoroacetone under these conditions.[84,85]

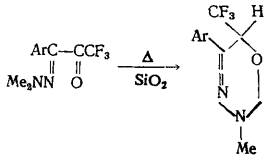
Methyl trifluoropyruvate, in a similar manner to hexafluoroacetone, can oxidise substituted tetrahydroquinoline:[84]



The reaction of hexafluoroacetone with tetramethyl-*p*-phenylenediamine stops at the stage where a CTC is formed.[28] On mixing the reactants the solution at first turns orange ("external complex") and after a few seconds it becomes blue ("internal complex").†

Dimethylaniline is attacked by hexafluoroacetone at the *para*-position,[89] in other words, its potential oxidation to a methyleniminium cation is suppressed by the competing electrophilic substitution in the benzene ring.

Intramolecular oxidation—reduction involving CF_3CO- and $CH_3N<$ groups—takes place on heating 1,1,1-trifluoro-3-arylpropan-2,3-dione phenylhydrazones, giving substituted oxadiazines:[90,91]



Hexachloroacetone, like hexafluoroacetone, proves to be sufficiently electrophilic to remove a hydride ion from triethylamine. However, the reaction does not stop when an iminium salt is formed. The iminium cation is deprotonated and the intermediate vinylamine is attacked by a second hexachloroacetone molecule with simultaneous haloform decomposition to give the aminovinylketone (XIV):[44]

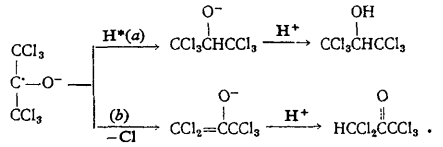
$$(CCl_3)_2CO + CH_3CH_2NEt_2 \rightarrow (CCl_3)_2CHOH + [CH_2{=}CHNEt_2],$$
$$(CCl_3)_2CO + [CH_2{=}CHNEt_2] \rightarrow CCl_3COCH{=}CHNEt_2 + CHCl_3.$$
$$\text{(XIV)}$$

¶Secondary heterocyclic amines are also oxidised by nitrobenzene (in the presence of transition metal salts).[87,88]

† Charge-transfer complexes and their corresponding terminology have been covered in three reviews.[23–25]

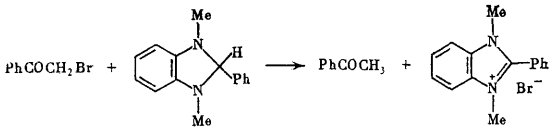
Diisopropylethylamine reacts in a similar manner, with only the ethyl group being oxidised.

When hexachloroacetone is treated with tri-n-propylamine, the product derived from replacing a chlorine atom by hydrogen—pentachloroacetone—is formed in addition to hexachloroisopropanol.[44] Talley[44] suggests that in this case hexachloroacetone acts as a chlorinating agent towards the enamine (compare the results of Laskovics and Schulman[92,93]). It cannot be excluded that both products are formed from a single intermediate—the hexachloroacetone radical anion—by the competing reactions of addition of a hydrogen atom (*a*) and elimination of a halogen atom (*b*):



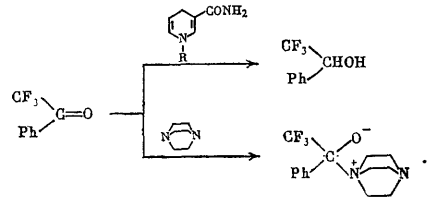
Tetramethyl-*p*-phenylenediamine forms a blue complex with hexachloroacetone;[28] pentachloroacetone and tetrachloroacetone are isolated from the reaction mixture.

An effective reagent for the reduction of α-halocarbonyl compounds which does not affect the carbonyl group is 1,3-dimethyl-2-phenylbenzimidazoline,[58] for example:

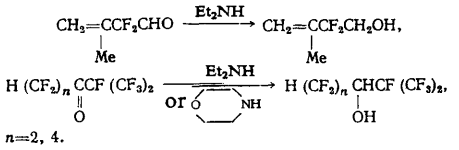


It is assumed that direct hydride transfer occurs in this case.

Trifluoroacetophenone, which is less active than hexafluoroacetone, is readily reduced by 1,4-dihydropyridine derivatives[26,27] but with triethylamine, quinuclidine and 1,4-diazabicyclo[2.2.2]octane it forms only betaines:[20]

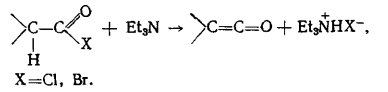


Cases are known where fluorine-containing carbonyl compounds are reduced by diethylamine. Thus, 2,2-difluoro-3-methyl-3-butenal[94] and polyfluoroalkyl heptafluoroisopropyl ketones[95] are converted to the corresponding alcohols:

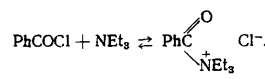


3. Anhydrides and halides of carboxylic acids

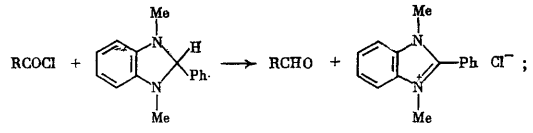
As has already been mentioned above, reactions of hydride transfer from tertiary amines compete with the direct addition of an electrophile to the amine, leading to ammonium salts. This has a particularly clear effect on the reactions of triethylamine with carboxylic acid halides. Thus, if the acid halide contains α-hydrogen atoms, dehydrohalogenation occurs, in other words, the amine acts as a base:[96]



With phosgene[97] and with carboxylic acid chlorides not containing α-hydrogen atoms[98–100] tertiary amines usually form acylammonium complexes, for example:



However, the very strong hydride ion donor—1,3-dimethyl-2-phenylbenzimidazoline—can reduce carboxylic acid chlorides to aldehydes:[58]



R = Ph, *p*-$O_2NC_6H_4$, *p*-$MeOC_6H_4$, n-C_7H_{15}, C_6H_{11}.

In addition, polyhalocarboxylic acid derivatives such as anhydrides,[101–103] acid chlorides,[46,102–105] and acid fluorides[104,105] contain a sufficiently electrophilic carbonyl carbon atom in their molecules that it can remove a hydride ion also from triethylamine.

Thus, acid halides are converted to aldehydes and the resulting diethylvinylamine is acylated by a second molecule of reactant to give aminovinyl ketones:

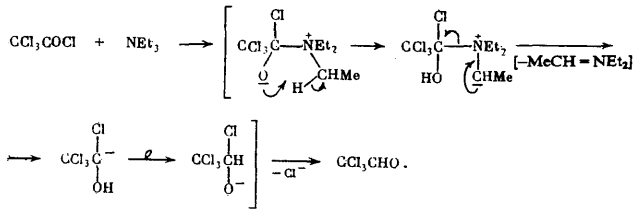
$$RCOX + NEt_3 \rightarrow RCHO + [CH_2{=}CHNEt_2],$$
$$RCOX + [CH_2{=}CHNEt_2] \rightarrow RCOCH{=}CHNEt_2,$$

R = CCl_3, CF_3, n-C_3F_7, iso-Pr; X = Cl, F.

The reaction is a convenient method for synthesising dialkylaminovinyl ketones, the yields of which are 30–90%. The aldehydes formed are usually not isolated since they are unstable under the reaction conditions. However, chloral is obtained in about 60% yield from trichloroacetyl chloride and perfluorobutyraldehyde is obtained (as its 2,4-dinitrophenylhydrazone) in 16% yield from perfluorobutyryl chloride.[104,105]

The reactions of carboxylic acid halides with tertiary amines most probably involve a single-electron transfer to form a CTC. Evidence in favour of this is the detection of characteristic absorption bands on mixing tetramethyl-*p*-phenylenediamine with trichloroacetyl chloride and also the coloration when diethylaniline, tributylamine, and other tertiary amines are added to trichloroacetyl chloride.[104,105]

Fraser and Swingle[46] suggest that the reduction of trichloroacetyl chloride with triethylamine involves the formation of an intermediate betaine:



They assume that the isolation of small quantities of ethylene and trichloroacetic acid diethylamide results from attack by the *O*-anion site in the betaine on to the β-hydrogen atom rather than the

α-hydrogen atom. However, these by-products could also be formed by decomposition of an acylammonium salt:[104]

$$RCONEt_3^+Cl^- \begin{cases} \longrightarrow RCONEt_2 + EtCl \\ \longrightarrow RCONEt_2 + CH_2{=}CH_2 + HCl \end{cases}$$

The formation of an acylammonium salt should not in principle inhibit reduction of the carbonyl group provided that there is an excess of amine reducing agent, since the electrophilicity of the carbonyl carbon atom in an acylammonium cation should be even higher than in the initial acid halide. In fact, when trichloroacetyl chloride is gradually added to an excess of triethylamine, an aminovinyl ketone is formed in about 90% yield. With the reverse order of mixing reactants, only trace amounts of the aminovinyl ketone are isolated and products derived from decomposition of the fairly unstable acylammonium salt—triethylamine hydrochloride, trichloroacetic acid diethylamide, and a considerable amount of tar—are mainly obtained:

$$CCl_3COCl + NEt_3 \begin{cases} \longrightarrow CCl_3COCH{=}CHNEt_2 \\ \longrightarrow CCl_3C^+(Cl)NEt_3Cl \rightarrow CCl_3CONEt_2 + EtCl + CH_2{=}CH_2 + NEt_3 \cdot HCl \end{cases}$$

Acid fluorides do not form acylammonium complexes (as a result of the high strength of the C–F bond) and the result of the reaction is virtually independent of the order of mixing the reactants.[104]

In the reaction of perfluoropivaloyl fluoride, carbon monoxide and monohydroperfluoroisobutane, which are products derived from the decomposition of the intermediate perfluoropivalaldehyde, are produced:[104,105]

$$(CF_3)_3CCOF \xrightarrow{NEt_3} \begin{cases} [(CF_3)_3CCHO] + (CF_3)_3COCH{=}CHNEt_2 \\ \longrightarrow (CF_3)_3CH + CO \end{cases}$$

α-Chlorohexafluoroisobutyryl fluoride reacts to form an aminovinyl ketone and a product in which the chlorine atom is replaced by hydrogen:[104,105]

$$(CF_3)_2CClCOF + NEt_3 \rightarrow (CF_3)_2CHCOF + (CF_3)_2CClCOCH{=}CHNEt_2.$$

A similar replacement of the bromine atom by hydrogen on treatment with triethylamine is known for bromides CF_3CXYBr (X, Y = CF_3, COOR).[106]

Tributylamine reacts with trichloroacetyl chloride in a similar manner to triethylamine:[104]

$$CCl_3COCl + EtCH_2CH_2NBu_2 \rightarrow CCl_3CHO + CCl_3COC(Et){=}CHNBu_2.$$

When trichloroacetyl chloride is reacted with trimethylamine, only products from the decomposition of the acylammonium salt are found.[104,105]

In the case of diethylaniline small quantities of aminovinyl ketone are formed, but the main reaction route, as also for dimethylaniline, proved to be acylation at the *para*-position of the benzene ring:[104,105]

$$CCl_3COCl + C_6H_4(NR_2) \begin{cases} \xrightarrow{R=Et} CCl_3COCH{=}CHN(Et)C_6H_4 \quad 7\% \\ \xrightarrow{R=Me,Et} CCl_3CO\text{–}C_6H_4\text{–}NR_2 \quad \sim 60\% \end{cases}$$

Perfluorobutyryl chloride also acylates diethylaniline at the *para*-position. Moreover, in both cases trace amounts of the corresponding triarylmethane dye—Ethyl Violet or Crystal Violet—are formed (see III.1).

Sources of perfluoroacyl fluorides in reactions with triethylamine can be provided by perfluoroolefin oxides,[104,105] which are known[107] to isomerise readily in the presence of catalytic quantities of tertiary amines

$$(CF_3)_2C\text{–}CF_2 \xrightarrow{NEt_3} (CF_3)_2CFCOF \xrightarrow{NEt_3} (CF_3)_2CFCOCH{=}CHNEt_2.$$

In a similar manner to perhalocarboxylic acid halides, trifluoromethanesulphenyl chloride can also oxidise triethylamine and undergo condensation with the resulting diethylvinylamine:[108]

$$CF_3SCl + CH_3CH_2NEt_2 \rightarrow (CF_3S)_2C{=}CHNEt_2.$$

In the presence of transition metal compounds as catalysts, perfluoroalkyl iodides also undergo a similar reaction.[109,110] Hydrolysis of the resulting amine (XV) gives an aminovinyl ketone or saturated and unsaturated fluorine-containing aldehydes:

$$R_FCF_2I + (RCH_2CH_2)_3N \xrightarrow{(Ph_3P)_4Pd} \rightarrow R_FCF_2C(R){=}CHN(CH_2CH_2R)_2 + R_FCF_2H + (RCH_2CH_2)_3N \cdot HI,$$

(XV)

$$(XV) \xrightarrow{H_2O} \begin{cases} \xrightarrow{(R=H)} R_FCOCH{=}CHNEt_2 \\ \longrightarrow R_FCF_2\text{–}CH(R)CHO \xrightarrow{-HF} R_FCF{=}CCHO \end{cases}$$

Zhou and Huang[109,110] propose a free-radical mechanism for this reaction as it is suppressed when *p*-dinitrobenzene and *p*-benzoquinone are added.

The photochemical reduction of various polyhaloalkanes with triethylamine also occurs by a free-radical mechanism.[111–113]

Trifluoroacetyl bromide phenylhydrazone (XVI) is reduced by triethylamine, with trifluoroacetaldehyde phenylhydrazone and diethylvinylamine being formed. The usual dehydrohalogenation to a nitrilimine occurs together with this; the latter undergoes a [3 + 2]-cycloaddition reaction with the vinylamine, and the subsequent elimination of diethylamine leads to a substituted pyrazole:[114]

$$CF_3C(Br){=}NNHPh \xrightarrow{NEt_3} \begin{cases} \longrightarrow CF_3CH{=}NNHPh + [CH_2{=}CHNEt_2] \\ \longrightarrow [CF_3C{\equiv}\overset{+}{N}\overset{-}{N}Ph] + Et_3N \cdot HBr \end{cases}$$

(XVI)

$$[CF_3C{\equiv}\overset{+}{N}\overset{-}{N}Ph] + [CH_2{=}CHNEt_2] \rightarrow \left[\begin{array}{c} CF_3 \\ \| \\ N \\ \diagdown\diagup \\ N\text{–}NEt_2 \\ | \\ Ph \end{array}\right] \xrightarrow{-Et_2NH} \begin{array}{c} CF_3 \\ \| \\ N \\ \diagdown\diagup \\ N \\ | \\ Ph \end{array}.$$

When bromide (XVI) is reacted with *N*-methylpyrrolidine, only a quaternary salt is formed and reduction is not found to occur:[114]

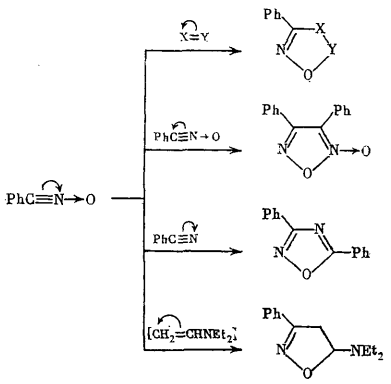
$$CF_3C(Br){=}NNHPh \xrightarrow{MeN} CF_3\text{–}C(=\overset{+}{N}(Me)\text{–}Br^-){=}NNHPh.$$

(XVI)

The oxidation of triethylamine to diethylvinylamine also occurs in the reaction with benzhydroxamoyl chloride (XVII).[115] The oxidising agent in this case is probably not acid chloride (XVII) but its dehydrochlorination product, a nitrile oxide, which is reduced to a nitrile. Thus, there are two dipolarophiles in the mixture—nitrile and enamine—which can compete for cycloaddition to the nitrile

oxide both with the separate addition of an "external" dipolarophile reagent and with the nitrile oxide itself:

$$PhC(Cl)=NOH + NEt_3 \rightarrow [PhC\equiv N \rightarrow O],$$
(XVII)
$$[PhC\equiv N \rightarrow O] + NEt_3 \rightarrow PhCN + [CH_2=CHNEt_2]$$



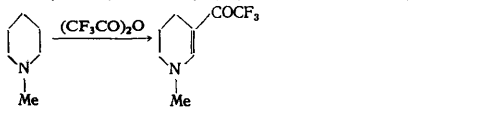
The ratio of products depends on the activity of the "external" dipolarophile, the quantity of trimethylamine, and the nature of the solvent.

In addition to acid chlorides, polyhalocarboxylic anhydrides are also readily reduced by tertiary amines, which is shown in the case of trifluoroacetic anhydride.[101,102] The resulting trifluoroacetaldehyde is isolated as acylal (XVIII). The intermediate enamine undergoes acylation, and in contrast to the reactions with acid chlorides, one[101] or both[102] hydrogen atoms can be replaced:

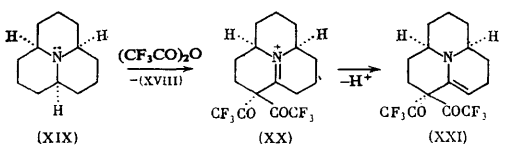
$$(CF_3CO)_2O + Et_3N \rightarrow \underset{\text{(XVIII)}}{(CF_3CO)_2C=CHNEt_2} + CF_3CH(OCOCF_3)_2 + CF_3COO^-\overset{+}{H}NEt_3.$$

Diisopropylethylamine reacts in a similar manner, with only the ethyl group being oxidised. In the case of methylpiperidine the heterocycle is oxidised:[102]

$$CH_3CH_2N(Pr\text{-}iso)_2 \xrightarrow{(CF_3CO)_2O} (CF_3CO)_2C=CHN(Pr(iso)_2 + CF_3COCH=CHN(Pr\text{-}iso)_2,$$



Diisopropylmethylamine is also oxidised by trifluoroacetic anhydride; in this case acylal (XVIII) is isolated but the product from conversion of the amine has not been studied. Treatment of the tricyclic amine (XIX) with trifluoroacetic anhydride gives acylal (XVIII) and the iminium salt (XX), which after treatment with base is isolated as enamine (XXI):[102]



(XIX) (XX) (XXI)

Schreiber[102] suggests various schemes for the mechanism of oxidation, including those that involve single-electron transfer. As the α-hydrogen atoms and unshared electron pair in amine (XIX) lie in different directions from the molecular plane, a mechanism via a cyclic transition state involving a betaine (see Section I) is impossible. However, elimination of a proton could occur on treatment with another amine molecule. Direct hydride transfer also cannot be excluded.

IV. Compounds containing other double bonds

1. Acylimines of fluoroketones

Acylimines of fluoroketones have clearly defined electrophilic activity. Moreover, cycloaddition reactions are typical for these compounds.[116] These properties are exhibited in reactions with tertiary amines.

Hexafluoroacetone benzoylimine readily reacts with triethylamine, oxidising it to diethylvinylamine.[117] When this intermediate reacts with the initial imine, a [4 + 2]-cycloaddition product is formed together with a linear product from addition to the C=N bond:

$$(CF_3)_2C=NCOPh + NEt_3 \rightarrow (CF_3)_2CHNHCOPh + [CH_2=CHNEt_2]$$

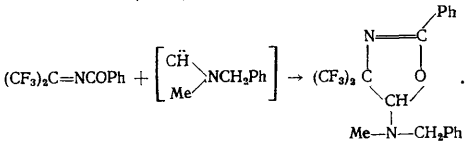
$$(CF_3)_2C=NCOPh + [CH_2=CHNEt_2] \rightarrow (CF_3)_2C\langle \text{CH}_2\text{—CH}(\text{NEt}_2)\text{—O—C(Ph)=N} \rangle + (CF_3)_2C(\text{NHCOPh})\text{CH=CHNEt}_2.$$

Hexafluoroacetone carbethoxyimine reacts with greater difficulty, forming only linear products:[117]

$$(CF_3)_2C=NCOOEt + NEt_3 \rightarrow (CF_3)_2CHNHCOOEt + (CF_3)_2C(\text{NHCOOEt})\text{CH=CHNEt}_2.$$

Benzyldimethylamine contains no β-hydrogen atoms in the molecule and the iminium cation that is formed at the first stage of the reaction is deprotonated to an aminocarbene which traps a second hexafluoroacetone benzoylimine molecule to form a [4 + 1]-cycloaddition product:[118]

$$(CF_3)_2C=NCOPh + Me_2NCH_2Ph \rightarrow (CF_3)_2\bar{C}HNCOPh\ \overset{CH_2}{Me}\!\!\gg\!\overset{+}{N}CH_2Ph \rightarrow$$
(XXII)
$$\rightarrow (CF_3)_2CHNHCOPh + \left[\begin{matrix}\ddot{C}H\\ Me\end{matrix}\!\!\gg\!NCH_2Ph\right],$$
(XXIII)



Exposure to visible light assists the formation of the aminocarbene (the oxidation stage—formation of the iminium salt—does not require light exposure, so this reaction cannot be classed as a photochemical oxidation). The addition of pyridine also accelerates the reaction.‡ The iminium salt (XXII) can be preserved in the dark for a long time but on heating it is converted to the reduction product (XXIII). The products derived from conversion of the amine have not been established in this case.

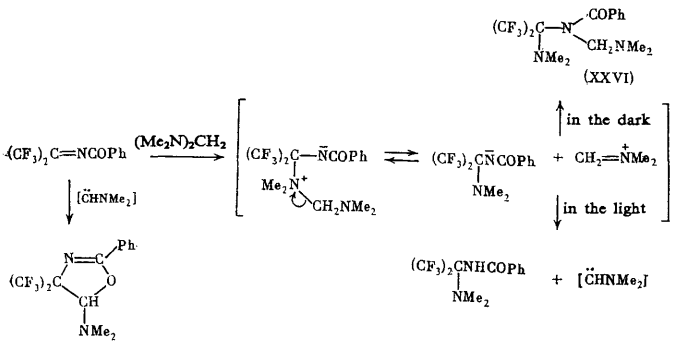
When hexafluoroacetone benzoylimine is reacted with bis-(dimethylamino)methane,[122] elimination of a dimethylaminomethyl group as a cationoid species also occurs together with hydride transfer (see II.1). As a result of hydride transfer, there is the formation of iminium salt (XXIV), which has been identified by

‡ For the generation of aminocarbenes by deprotonation of iminium cations, see the studies of Böhme et al.[7,119,121] Another route for the formation of an aminocarbene from a tertiary amine is dehydrofluorination of α,α-difluorotrimethylamine (see also II.1). The carbene Me_2NCF: undergoes cycloaddition with two moles of hexafluoroacetone to form a substituted dioxolane.[64]

NMR spectroscopy. When this salt is treated with an alcohol it is converted to *N*-benzoylhexafluoroisopropylamine (XXV):

$$(CF_3)_2C{=}NCOPh + (Me_2N)_2CH_2 \rightarrow$$
$$\rightarrow \underset{\text{(XXIV)}}{(CF_3)_2CH\bar{N}COPh\ \overset{+}{C}H(NMe_2)_2} \xrightarrow{ROH} \underset{\text{(XXV)}}{(CF_3)_2CHNHCOPh}.$$

The second reaction route is formation of a betaine followed by dissociation to an anion and the dimethylaminomethyl cation. Subsequently addition occurs in the dark with the formation of triamine (XXVI) while in the light the dimethylaminomethyl cation is deprotonated to dimethylaminocarbene, which traps a second molecule of hexafluoroacetone benzoylimine and a [4 + 1]-cycloaddition product is obtained as a result:



Thus in this reaction bis(dimethylamino)methane serves as the source of a hydride ion, dimethylaminomethyl cation, and dimethylamiocarbene.

The molecule of hexafluoroacetone perfluoropivaloylimine (XXVII) contains a perfluoro-t-butyl group which is readily eliminated as an anion.[16] This property, as a rule, determines the course of the reactions of imine (XXVII).

Benzyldimethylamine donates a hydride ion to imine (XXVII), the resulting iminium salt having been identified by ^{19}F NMR spectroscopy. The cation of the iminium salt then combines with the perfluoro-t-butyl anion being eliminated, as a result of which amine (XXVIII) and monohydroperfluoroisopropyl isocyanate (XXIX) are obtained:[123]

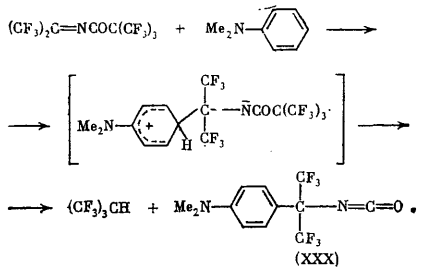
$$\underset{\text{(XXVII)}}{(CF_3)_2C{=}NCOC(CF_3)_3} + Me_2NCH_2Ph \rightarrow (CF_3)_2CH\bar{N}COC(CF_3)_3\ \overset{CH_2}{\underset{Me}{\overset{+}{N}}}CH_2Ph \rightarrow$$
$$\rightarrow \underset{\text{(XXIX)}}{(CF_3)_2CHN{=}C{=}O} + \underset{\text{(XXVIII)}}{(CF_3)_3CCH_2\overset{Me}{\overset{|}{N}}CH_2Ph}$$

Triethylamine also reacts as a hydride ion source with imine (XXVII); in this case isocyanate (XXIX) and monohydroperfluoroisobutane $(CF_3)_3CH$ are isolated.

When bis(dimethylamino)methane reacts with imine (XXVII) it acts only as a source of the dimethylaminomethyl cation; hydride transfer was not found to occur:[122]

$$\underset{\text{(XXVII)}}{(CF_3)_2C{=}NCOC(CF_3)_3} + Me_2NCH_2NMe_2 \rightarrow \left[(CF_3)_2C(\bar{N}COC(CF_3)_3)\overset{+}{N}Me_2CH_2NMe_2\right] \rightarrow$$
$$\rightarrow (CF_3)_3CCH_2NMe_2 + \left[(CF_3)_2C(NMe_2)N{=}C{=}O\right] \rightarrow \underset{CF_3}{\overset{CF_3}{\overset{|}{C}}}{=}N{-}C(=O)NMe_2.$$

Dimethylaniline is attacked by imine (XXVII) at the *para*-position of the benzene ring; elimination of monohydroperfluoroisobutane yields isocyanate (XXX):[123]



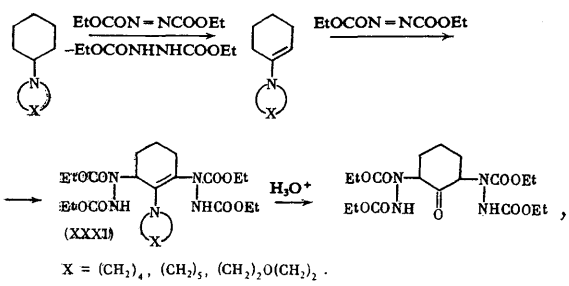
2. Azo compounds

Reactions of tertiary amines with dibenzoyldiimide and diethyl azodicarboxylate resemble the corresponding reactions with hexafluoroacetone benzoylimine. Azo compounds give the reduction products—dibenzoylhydrazine and diethyl hydrazodicarboxylate—in high yield, and the intermediate enamine reacts with the initial azo compound to give either vinyl substitution products of [2 + 4]-cycloaddition products.

Thus, diethyl azodicarboxylate reacts with triethylamine to form a product derived from double substitution in the intermediate enamine:[124]

$$EtOCON{=}NCOOEt + NEt_3 \rightarrow EtOCONHNHCOOEt + [CH_2{=}CHNEt_2],$$
$$EtOCON{=}NCOOEt + [CH_2{=}CHNEt_2] \rightarrow \underset{EtOCONHN}{\overset{COOEt}{\diagdown}}C{=}CHNEt_2.\ \underset{EtOCONHN}{\overset{COOEt}{\diagdown}}$$

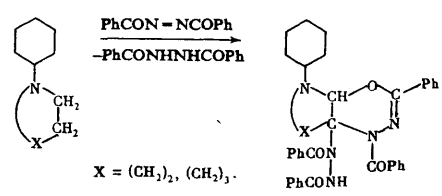
The cyclohexane ring is oxidised in *N*-cyclohexyl-substituted pyrrolidine, piperidine, and morpholine.[124] The azo compound attacks the intermediate enamine to form bis-hydrazines (XXXI):



X = $(CH_2)_4$, $(CH_2)_5$, $(CH_2)_2O(CH_2)_2$.

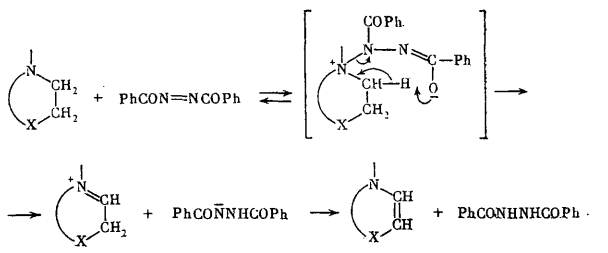
Acid hydrolysis gives a 2,6-disubstituted cyclohexanone. The formation of 2,6-disubstituted compounds (XXXI) is due to the known[125] migration of the double bond in enamines of this type.

Treatment with benzoyldiimide, on the other hand, leads to oxidation of the heterocycle rather than the carbocycle.[45] The resulting enamine reacts with two molecules of initial azo compound to give a product which corresponds to two reaction routes occurring at the same time—replacement of a vinyl hydrogen atom and cycloaddition:

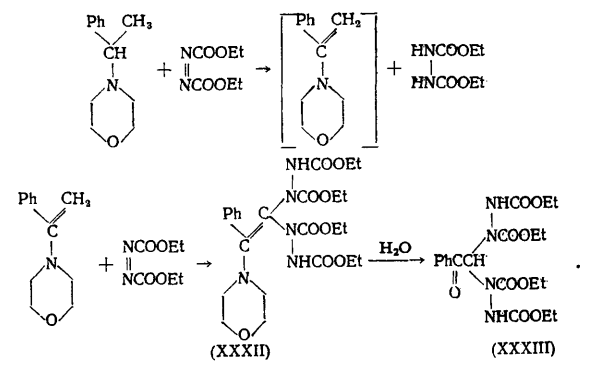


X = $(CH_2)_2$, $(CH_2)_3$.

The variation in oxidation route is attributed to the different mechanisms of these reactions.[45] For diethyl azodicarboxylate a mechanism via the formation of an intermediate CTC and free radicals (styrene added to the reaction mixture undergoes 20% conversion to polystyrene) has been suggested, while for dibenzoyldiimide a mechanism via a betaine has been proposed:

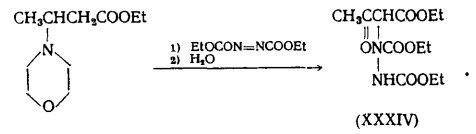


Marchetti[45] considers this to be the explanation for the different behaviour of *N*-cyclohexylmorpholine. Dibenzoyldiimide, in contrast to diethyl azodicarboxylate, does not react with this amine. This appears natural as the basicity of morpholine is less than the basicity of pyrrolidine and piperidine by a factor of 10^3, so the formation of a betaine is inhibited. *N*-(α-Methylbenzyl)morpholine also does not react with dibenzoyldiimide but reacts with diethyl azodicarboxylate.[124] As a result, adduct (XXXII) is formed, and after hydrolysis ketone (XXXIII) is obtained:



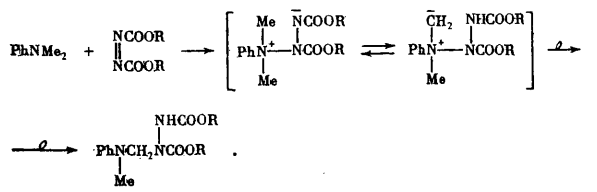
The same product is obtained when starting from a known sample of α-morpholinostyrene.

The hydrazine-substituted ethyl acetoacetate (XXXIV) is obtained in a similar manner from ethyl β-morpholinobutyrate:[124]



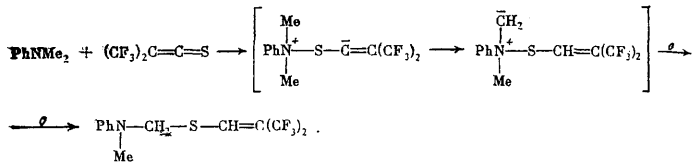
N-Ethylpiperidine, *N*-methylcyclohexylamine, and *N,N*-diethylaniline also reduce diethyl azodicarboxylate.[124] The products derived from dehydrogenation of the amines were not isolated, but after acid hydrolysis piperidine was found in the reaction mixture in the case of *N*-ethylpiperidine and *N*-ethylaniline was found in the case of *N, N*-diethylaniline.

Dimethylaniline adds on to azodicarboxylate esters with cleavage of a C–H bond in a methyl group. An ionic mechanism via a betaine and ylide rearrangement has been proposed:[126]



This reaction can also be interpreted as a hydride transfer followed by addition of the iminium cation to the aza anion.

Dimethylaniline adds on to bis(trifluoromethyl)thioketene in a similar manner:[127]



The mechanism of this reaction is evidently ionic; it is not suppressed by the addition of diphenylpicrylhydrazyl and is retarded by the introduction of electron-withdrawing substituents into the benzene ring of the amine. A similar addition of ethers to bis(trifluoromethyl)thioketene is sensitive to the addition of peroxides, so the reaction with ethers is possibly a free-radical reaction.[127] Thus, the mechanism of these reactions can vary fundamentally with small changes in the nature of the reactants.

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It is clear from the material presented here that the reduction of unsaturated electrophilic compounds by amines (usually tertiary) occurs quite widely in organic chemistry. In certain cases such reactions are of importance synthetically, and further progress is to be expected in this direction. The study of reactions of this type is increasingly important because they are proving to be undesirable as they can compete with "normal" reactions in which amines are used, for example, as basic catalysts. The authors hope that the present review will to some extent stimulate research in this field.

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