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THE CHEMISTRY OF MAGNESYLAMINES†

P.A.Petyunin

COMPOUNDS

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INTRODUCTION

Magnesylamines are derivatives of nitrogenous compounds in which the nitrogen is joined to magnesium subhalide (MgX). They were first prepared by Meunier[1] in 1903 by the reaction of primary and secondary amines with Grignard reagents:

$$RNH_2+R'MgX \longrightarrow RNHMgX+R'H,$$
$$R_2NH+R'MgX \longrightarrow R_2NMgX+R'H.$$

In primary amines magnesium subhalide may substitute both hydrogen atoms with the formation of dimagnesylamines[2]:

$$RNH_2+2R'MgX \longrightarrow RN(MgX)_2+2R'H$$

Unsubstituted magnesylamine may be prepared by the reaction of Grignard reagents with ammonia, ammonium chloride[3], and chloramine[4,5]:

$$RMgX+NH_3 \longrightarrow RH+H_2NMgX,$$
$$2RMgX+NH_4Cl \longrightarrow 2RH+MgClX+H_2NMgX,$$
$$RMgX+NH_2Cl \longrightarrow RCl+H_2NMgX.$$

† Aminomagnesium halides (Ed. of Translation).

In the last case primary amines can also be formed:

$$RMgX+NH_2Cl \longrightarrow RNH_2+MgXCl.$$

The reaction depends to a large extent on the nature of the halogen in RMgX: chlorides favour the formation of amines and iodides that of the magnesylamine.

Apart from the mixed magnesylamines, symmetrical diaminomagnesium compounds, obtained by the reaction of amine with activated magnesium[6,7],

$$2RNH_2+Mg \longrightarrow H_2+(RNH)_2Mg,$$

are also known. However, they have not found wide applications.

Present developments in the chemistry of magnesylamines are concerned with increasing their application in organic synthesis and with studies on new nitrogenous compounds. About 100 different magnesylamines are now known and their number is increasing continuously. They resemble Grignard reagents in their reactivity and like them find wide application in organic syntheses.

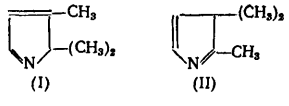
Since they are more nucleophilic than amines, they react under milder conditions and can yield compounds which cannot be prepared from free amines.

They are particularly important in the chemistry of certain heterocycles (pyrrole, indole), where they can be used for the synthesis of alkyl-derivatives, aldehydes, ketones, acids, and esters. They have been used to synthesise certain 3-, 4-, 5-, and 6-membered heterocyclic systems, alkaloids, vitamin A, and anaesthetics. They have proved to be excellent catalysts for the ketol condensation of ketones.

The time is now ripe for a general review of the chemistry of these compounds.

1. REACTIONS WITH HALOGENO-DERIVATIVES

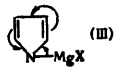
Reactions between magnesylamines and halogeno-derivatives yield products with various degrees of substitution. Thus when methyl iodide reacts with pyrrolylmagnesium bromide 2, 2, 3-trimethyl-2*H*-pyrrole (I) and 2, 3, 3-trimethyl-3*H*-pyrrole (II) are obtained[8]:



(I) (II)

A mixture of monoethyl- and dimethyl-pyrroles is formed in the reaction between pyrrolylmagnesium bromide and ethyl halide[9,10]. As a rule, pyrrolylmagnesium halide yields *C*-derivatives and only in certain cases can *N*-derivatives be obtained: the structure of these compounds was the subject of a lively discussion[9,11-14].

It can now be regarded as established that pyrrolylmagnesium halide has an Mg–N bond. This is confirmed by experiments on the determination of the active hydrogen atom in pyrrole[15] and by the inability of *N*-methylpyrrole to form a true Grignard reagent[16]. According to Nesmeyanov[17] pyrrolylmagnesium halide possesses two types of reactivity and its structure may be represented by formula (III):

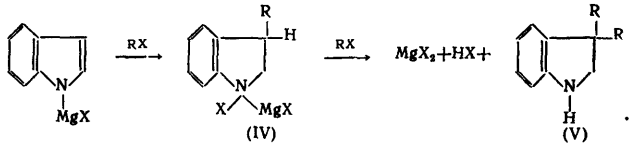


(III)

Reaction of imidazolylmagnesium bromide with methyl and ethyl iodides yields 1, 2-dimethyl- and 1, 2-diethyl--imidazoles[18].

Reaction with indolylmagnesium halide results in the formation of 3-alkyl-derivatives of indole[19].

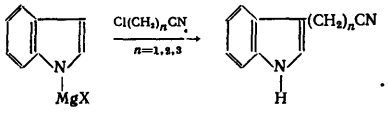
Majima and Hoshino[20] at first proposed a radical mechanism for their reaction, but later Hoshino[21] adopted a mechanism involving 1, 3-addition of alkyl halide to the pyrrole nucleus of indole:



(IV) (V)

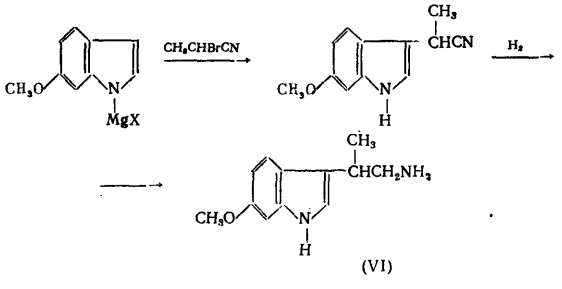
Apart from 3, 3-dialkylindoline (V), 3-alkyl-derivatives of indole can be obtained, through hydrolysis of compound(IV).

Reaction between halogeno-nitriles and indolylmagnesium halide has assumed considerable importance for the synthesis of biologically active compounds[22-25]:



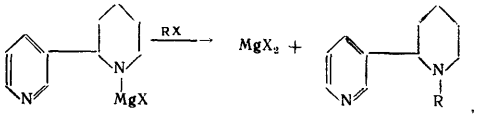
On hydrolysis of the resulting nitriles β-indolylcarboxylic acids — plant growth hormones — are obtained.

According to a patent[26], 2-(6′-methoxyindol-3′-yl)-1--propylamine (VI), which is an intermediate in the synthesis of physiologically active reserpine-like compounds, is obtained in the following way:



(VI)

Orekhov and Norkina[27] successfully employed the reaction between anabasylmagnesium iodide and alkyl halides for the synthesis of *N*-alkyl derivatives of anabasine (yield 50–60%):



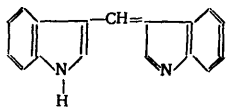
where R = CH_3, C_2H_5, $CH_2=CH-CH_2$, $C_6H_5CH_2$.

Methods based on magnesylamines have been developed for the synthesis of trimethylhydrazine (yield 25%)[28] and azino-derivatives of ketones (yield 57%)[29]:

$$CH_3NH-N(MgI)CH_3+CH_3I \longrightarrow MgI_2+CH_3NH-N(CH_3)_2,$$

$$2(C_6H_5)_2C=NMgBr+I_2 \longrightarrow 2MgBrI + (C_6H_5)_2C=N-N=C(C_6H_5)_2.$$

A complex reaction between indolylmagnesium bromide and carbon tetrachloride results in the formation of indol-3-yl(2*H*-indolyl-3-yl)methane[30]:



2. REACTIONS WITH NITRILES

Reaction between magnesylamines and nitriles results in the formation of amidines (yield 24–58%)[31]:

$$RCN \xrightarrow{R'NHMgX} RC(=NMgX)NHR' \xrightarrow{H_2O} Mg(OH)X + RC(=NH)NHR',$$

where R = n-C_4H_9, C_6H_5, *p*-$CH_3OC_6H_4$; R′ = H, CH_3, C_6H_5, $C_6H_5CH_2$.

Diphenylaminomagnesium bromide does not react with benzonitrile, probably because of steric hindrance, and benzyl cyanide yields α-cyano-β-imino-α, γ-diphenylpropane in 81% yield instead of the corresponding amide:

$$C_6H_5{-}CH_2CN \xrightarrow{R_2NMgX} C_6H_5CH{=}C{=}NMgX \xrightarrow{C_6H_5CH_2CN}$$

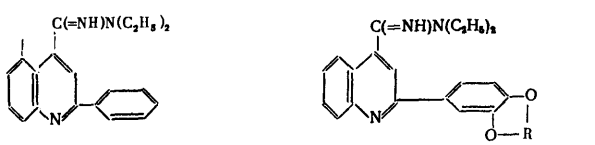
$$\longrightarrow C_6H_5{-}CH_2{-}\underset{\underset{NMgX}{\|}}{C}{-}CH(CN)C_6H_5 \xrightarrow{H_2O} C_6H_5CH_2C{-}CH(CN)C_6H_5.$$
$$\underset{NH}{\|}$$

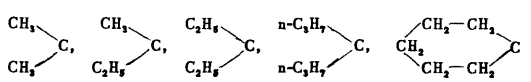
Under the same condition diethylcyanamide yields a guanidine derivative in 58% yield:

$$(C_2H_5)_2NCN \xrightarrow{(C_2H_5)_2NMgX} (C_2H_5)_2NC(=NMgX)N(C_2H_5)_2 \xrightarrow{H_2O}$$

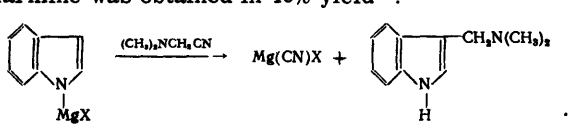
$$\longrightarrow (C_2H_5)_2NC(=NH)N(C_2H_5)_2 + Mg(OH)X.$$

Lusinhi *et al.*[32] employed the reaction between diethylaminomagnesium bromide and nitriles of substituted 2-phenylquinoline-4-carboxylic acids for the synthesis of pharmacologically active *NN*-diethylamidines of 2-(3′, 4′-dialkylmethylenedioxyphenyl)quinoline-4-carboxylic acids (yields 52–97%):

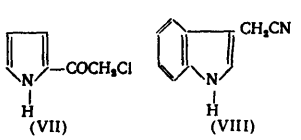


where R = 

Like alkyl halides, certain nitriles enter into exchange reactions. Thus when indolylmagnesium halide was allowed to react with dimethylaminoacetonitrile, the alkaloid harmine was obtained in 40% yield[33]:



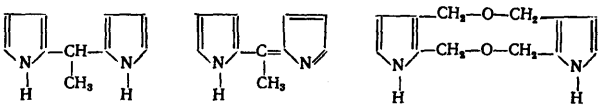
It is interesting that chloroacetonitrile behaves differently with pyrrolylmagnesium and indolylmagnesium halides, yielding 2-chloroacetylpyrrole (VII) with the first[34], and (3-indolyl)acetonitrile (VIII) with the second[23]:



(VII) (VIII)

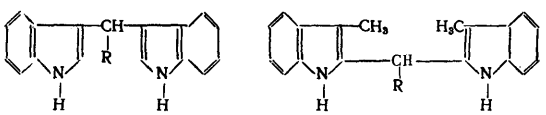
3. REACTIONS WITH ALDEHYDES, KETONES, AND QUINONES

The reaction of aldehydes and ketones with heterocyclic magnesium halide derivatives was mainly studied. It was established that pyrrolylmagnesium halide yields two products with acetaldehyde: 2, 2′-ethylidenedipyrrole (IX) and 2-[1-(2-pyrrolyl)ethylidene]-2*H*pyrrole (X)[35,36]; with formaldehyde the cyclic diether (XI) derived from 2, 3-di(hydroxymethyl)-pyrrole is formed[37]:



(IX) (X) (XI)

The ability to replace the aldehyde oxygen with two indolyl radicals is more clearly shown in reactions with indolylmagnesium halide. As a result 3,3′-alkylidene- or 3, 3′-arylidenediindoles (XII) are formed (yield up to 60%)[38–40]; when the β-position is occupied, the product is 2, 2′-arylidenebis(3-methylindole) (XIII)[38–40]:



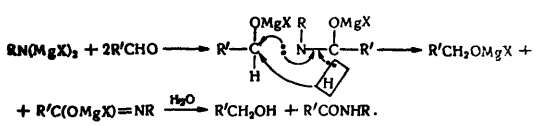
(XII) (XIII)

With benzaldehyde, aminomagnesium halide (NH_2MgX) yields hydrobenzamide and ammonium benzoate[3] and hydrazobenzene-*NN*′-dimagnesium iodide yields dibenzoylhydrazobenzene[41].

Reaction between the magnesium derivative of phenylurethane and benzaldehyde results in the formation of phenyl-α-hydroxybenzylurethane[42]:

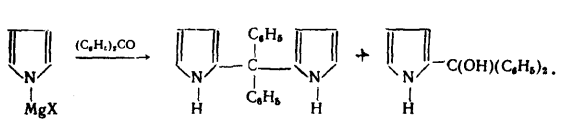
$$C_6H_5N(MgBr)COOC_2H_5 \xrightarrow{C_6H_5CHO} C_6H_5CHOHN(C_6H_5)COOC_2H_5.$$

Unlike the monomagnesylamines, dimagnesylamines react in 1:2 ratio with aromatic aldehydes with the formation of aromatic amides and alcohols[43]. The highest yields (50–90%) are obtained when the reaction is carried out in pyridine or dioxane[44]. The reaction is of the oxidation–reduction type and apparently proceeds as follows[45]:



The importance of steric hindrance in this reaction has been investigated[46].

Chelintsev *et al.*[47] showed that in ketones the carbonyl oxygen can be either replaced by two radicals with the formation of hydrocarbons (XIV) or can add on one molecule of magnesylamine halide, the corresponding substituted methanol (XV) being then formed:

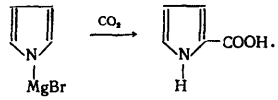


(XIV) (XV)

Reactions of magnesylamines with various ketones[39,47–49] and with anthraquinone and phenanthroquinone[50,51] have been described.

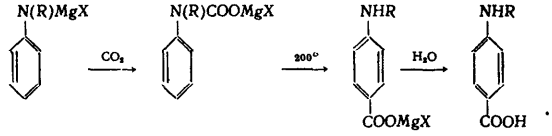
4. CARBOXYLATION

Reaction between a magnesylamine and carbon dioxide results in the formation of carboxylic acids, an important reaction for syntheses in the heterocyclic series. Thus pyrrolylmagnesium bromide and its derivatives with at least one free α-position yield α-pyrrolecarboxylic acids[52-55]:

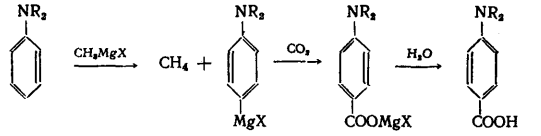


The carboxyl group enters at the β-position when both α-positions are occupied[56,57] or when the reaction is carried out at 250°–270°.[39] Indolylmagnesium halide gives 3-indolecarboxylic acid[39,53], and when the β-position is occupied, 1- and 2-indolecarboxylic acids[53].

Houben and his coworkers[58-60] proposed a method for the preparation of aromatic amino-acids (yield 50%):



p-Dialkylaminobenzoic acids are synthesised as follows[59]:



Primary aromatic amines do not give acids, since instead of rearrangement the carbamate undergoes conversion to diarylurea[58]:

$$2C_6H_5NHCOOMgX \longrightarrow C_6H_5NHCONHC_6H_5 + MgCO_3 + MgX_2.$$

Carboxylation of diphenylaminomagnesium iodide[61], hydrazobenzene-*NN'*-dimagnesium halide[41], and magnesium derivatives of aromatic amines[6,7] has been described.

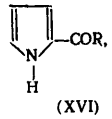
5. REACTIONS WITH ACID CHLORIDES AND ANHYDRIDES, ESTERS, AND LACTONES

Magnesylamines react in equimolar proportions with acid chlorides with the formation of amides:

$$RNHMgX + R'COX \longrightarrow MgX_2 + RNHCOR'.$$

With benzoylchloride aminomagnesium iodide gives benzamide[3], anilino-*NN*-dimagnesium halide gives dibenzoylaniline[2], hydrazobenzene-*N,N'*-dimagnesium halide gives *NN'*-dibenzoylhydrazobenzene[41], and ethoxycarbonylaminomagnesium bromide gives benzoylurethane[62].

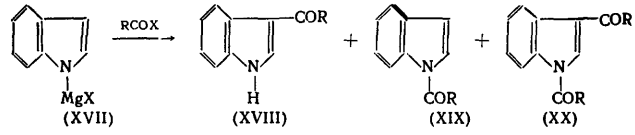
Reaction between magnesylamines, obtained from heterocycles with a secondary nitrogen atom in the ring, and acid halides yields ketones or *N*-acyl derivatives. This reaction constitutes the principal method for the synthesis of the ketones of certain heterocycles (pyrrole, indole). Thus when pyrrolylmagnesium halide reacts with acid chlorides, α-alkyl(aryl)pyrrole ketones (XVI) are formed in yields up to 80%[63-68]:



(XVI)

where R = CH_3, $CHCl_2$, CCl_3, C_2H_5, CH_3CHCl, n-C_3H_7, C_6H_5, $C_6H_5CH_2$, , , and . In the reaction of homologues of pyrrolylmagnesium halide the acyl group enters at an α-position, and when these are occupied, at a β-position[69,70].

Indolylmagnesium halide (XVII) yields 3-acyl derivatives (XVIII) and very small quantities of *N*-acyl (XIX) and 1, 3-diacyl derivatives (XX)[71]:



The quantity of (XIX) increases when the temperature is lowered. If a substituent is present at the β-position of (XVII), the acyl group enters at the α-position[72].

Pyrrolylmagnesium and indolylmagnesium halides react with dicarboxylic acid halides to form diketones[73-75]; with the acid chlorides of the corresponding ethyl half-esters, esters of keto-acids are formed[70,76-80].

Reaction between imidazolylmagnesium halide and acid halides yields alkyl-2-imidazolylketones[81], *N*-acyl derivatives being formed in the reaction between acid halides and magnesylamines derived from pyrazole[78,82,83], benzoimidazole[84], carbazole[61,85], and phenothiazine[86].

In the reaction between acid halides and magnesium halide derivatives of ketimines (intermediates in the reaction between nitrile and alkylmagnesium compounds) *N*-acyl derivatives of the ketimines were isolated[87]:

$$C_6H_5CN \xrightarrow{RMgX} C_6H_5RC{=}NMgX \xrightarrow{R'COX} C_6H_5RC{=}NCOR',$$

where R = C_2H_5, iso-C_4H_9; R' = CH_3, n-C_3H_7, iso-C_4H_9, and C_6H_5.

Acid anhydrides react similarly to the halides[88,89].

The reaction between magnesylamines and esters was first studied by Bodroux[90,91]. Its mechanism can be represented as follows:

$$2RNHMgX + R'COOR'' \longrightarrow (RNH)_2CR'OMgX + Mg(OR'')X,$$
$$(RNH)_2CR'OMgX \xrightarrow{H_2O} RNH_2 + Mg(OH)X + RNHCOR'.$$

It is evident that only half of the amine employed is converted to the amide, the second half not reacting. According to Bassett and Thomas[92], the reaction proceeds in equimolar proportions with the formation of the complex (XXI):

$$RCOOR' + R''NHMgX \longrightarrow \underset{(XXI)}{RC(NHR'')(OR')OMgX}.$$

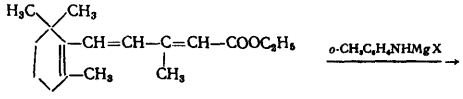
The role of the second molecule of the magnesylamine is to decompose the complex (XXI) and thus ensure the maximum yield of the reaction product. Later the Bodroux reaction was extended to esters of aromatic acids[95], halogeno-[93,94], and hydroxy-acids[86], and dicarboxylic acids[91].

Esters of chloroformic acid yield the corresponding carbamates[61]:

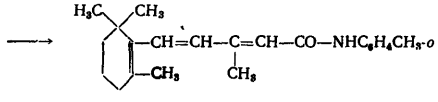
$$R_2NMgX + ClCOOC_2H_5 \longrightarrow MgXCl + R_2NCOOC_2H_5.$$

The reaction is exceptionally important in the chemistry of heterocyclic compounds since it gives the esters of the corresponding carboxylic acids in 70–80% yields. Numerous examples of this reaction are quoted in Fisher and Orth's monograph[97]. The esters of carbamic acid are also obtained when magnesylamines react with carbonic acid esters[13].

The Bodroux reaction has acquired considerable importance for the synthesis of natural polyenes (vitamin A). Kuhn and Morris[98] used it to convert the ester of β-ionylideneacetic acid (XXII) to the corresponding toluidide (XXIII), from which β-ionylideneacetaldehyde, the starting material for the synthesis of vitamin A, was obtained by the method of Braun and Rudolph[99]:



(XXII)



(XXIII).

Good results were also obtained in the synthesis of certain local anaesthetics[100,101].

Dimagnesylamines react in equimolar proportions with esters, which ensures the most complete utilisation of the amine, the yield of the aromatic amides increasing twofold[2]:

$$RCOOR' + R''N(MgX)_2 \longrightarrow Mg(OR')X + RC(OMgX)=NR'' \xrightarrow{H_2O} Mg(OH)X + RCONHR''.$$

Later this reaction was employed for the synthesis of aromatic amides of 9-hydroxyfluorene-9-carboxylic[102], mandelic[103], anthranilic[104], and *N*-substituted anthranilic acids[105].

Berdinskii and Mityanin[106] developed a method for the preparation of unsymmetrical diphenylhydrazides of carboxylic acids by allowing esters to react with diphenylhydrazo-*NN*-dimagnesium bromide (yield 70–94%):

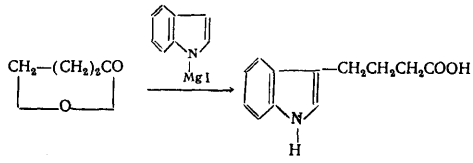
$$(C_6H_5)_2N{-}N(MgX)_2 + RCOOR' \longrightarrow Mg(OR')X +$$

$$+ RC(OMgX)=N{-}N(C_6H_5)_2 \xrightarrow{H_2O} Mg(OH)X + RCONHN(C_6H_5)_2,$$

where R = CH_3, n-C_3H_7, C_6H_5, $C_6H_5CH=CH$, *o*-HOC_6H_4.

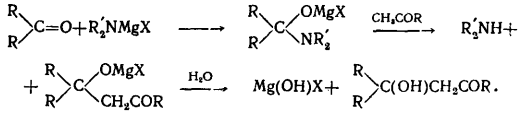
The reaction of magnesylamines with esters of heterocyclic compounds was first studied by Chelintsev and Terent'ev[12]. They established that the reaction proceeds in equimolar proportions with the formation of aldehydes and ketones: aldehydes are formed in the reaction with formic acid ester (yield 28%)[107] and ketones with esters of other acids (yield 50–60%)[108]. *N*-Acyl derivatives can also be obtained, their formation being favoured by low reaction temperature. Putokhin[109] studied in detail the effect of temperature on the reaction between indolylmagnesium halide and esters, and examined the mechanism of this reaction.

Among the lactones, only the reaction of butyrolactone, which with indolylmagnesium halide yields γ-(3-indolyl) butyric acid, was studied[110]:



6. CONDENSATION REACTIONS

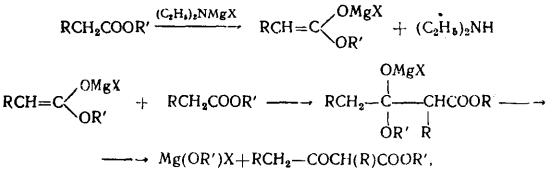
(a). Ketol condensation. Magnesylamines have proved to be excellent condensing agents for this reaction of ketones. They have made it possible to condense pinacolones and also aromatic and acyclic ketones, which enter into this reaction either with considerable difficulty or even not at all[111-113]. The condensing agents may be magnesylamines derived from primary and secondary aromatic amines. Aliphatic amines, however, are less suitable since in their presence yields are reduced from 70–80 to 10%[114]. The reaction proceeds as follows:



It has been employed for the condensation of the same and two different ketones[111-117].

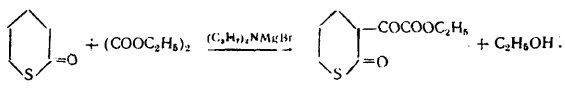
Chelintsev and Pataraya[117] established that, depending on the ease of removal of the hydroxyl group, unsaturated ketones may be obtained together with the ketols.

(b). Ester condensation. Hauser and Walker[118] found that magnesylamines can catalyse ester condensation. The reaction proceeds rapidly and with high yield of β-keto-acid esters (up to 75%). Diethylaminomagnesium bromide proved to be the best reagent for this purpose. The authors proposed the following reaction scheme:



where R = H, CH_3, CH_3CH_2, C_6H_5; R' = C_2H_5, $C_6H_5CH_2$. Good results were also obtained in mixed ester condensation.

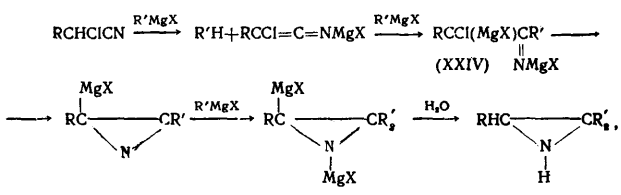
A disadvantage of the method is the fact that apart from ester condensation a competing amide-forming reaction may also occur. For example, in the case of isobutyric and isovaleric acid esters the amides of the initial acids were obtained instead of the β-keto-acid esters. Korte and Buchel[119] successfully employed diisopropylaminomagnesium bromide in the condensation of δ-thiovalerolactone with oxalic acid ester; α-ethoxyoxalyl-δ-thiovalerolactone was obtained in 74% yield:



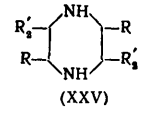
Thus magnesylamines have proved to be extremely active condensing agents.

7. USE OF MAGNESYLAMINES FOR THE SYNTHESIS OF HETEROCYCLES

Magnesylamines have found application in the synthesis of heterocyclic compounds. Thus ethyleneimine derivatives are obtained when Grignard reagents react with α-chloro-nitriles[120,121]:

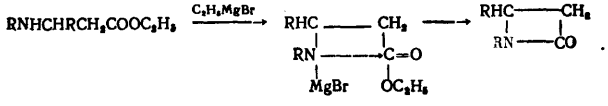


where R and R′ = C_2H_5; R = C_3H_7, R′ = C_2H_5; R = iso-C_4H_9, R′ = C_2H_5. The ethyleneimine ring closes when magnesium halide is split out from the ketimine derivative (XXIV). Together with the ethyleneimine derivative, a dimeric product, a piperazine derivative (XXV), is also formed:



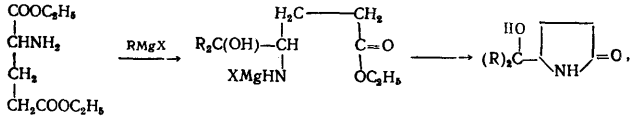
(XXV)

A method for the preparation of β-lactams, based on the cyclisation of β-amino-acid esters, has been developed[122,123]. The reaction proceeds *via* a stage in which an *N*-magnesium bromide derivative of the ester is formed, which increases the electron density at the nitrogen atom and facilitates the closure of the β-lactam ring:



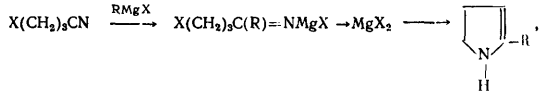
This method was developed further in studies on the synthesis of penicillin and was used for the preparation of a number of azetidines which are structurally related to penicillin[124]. A disadvantage of the method is the intermolecular formation of open-chain amides together with β-lactam cyclisation. This occurs particularly in experiments with unsubstituted esters of β-amino-acids. Thus unsubstituted 2-azetidinone was obtained in only 0.76% yield[125].

Under the action of Grignard reagents ethyl glutamate cyclises to yield pyrrolidone derivatives[126]:



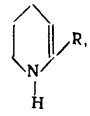
where R = CH_3, C_2H_5, n-C_4H_9, C_6H_5, $C_6H_5CH_2$.

γ-Halogeno-nitriles were employed for the synthesis of pyrroline derivatives (yield 41–69%)[127-132]:



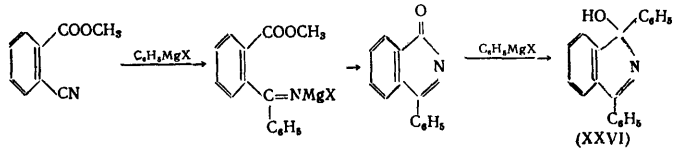
where R = C_2H_5, C_6H_{11}, C_6H_5, $C_6H_5CH_2$, *o*(*m*,*p*)-$CH_3C_6H_4$. Pyrrolines are also obtained in a small yield (11%) when Grignard reagents act upon γ-phenoxybutyronitrile[131].

Similarly δ-chlorovaleronitrile readily yields α-substituted tetrahydropyridine derivatives (yield 22–66%)[133]:

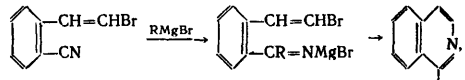


where R = n-C_4H_9, C_6H_{11}, C_6H_5, *p*-ClC_6H_4, *p*-$CH_3C_6H_4$.

All these reactions proceed *via* a stage in which magnesylamines are formed. Magnesylamines function as intermediates in the conversion of methyl *o*-cyanobenzoate to 1-hydroxy-1, 3-diphenylisoindole (XXVI) (yield 90%)[134] and of *o*-cyano-ω-bromostyrene to isoquinoline derivatives (XXVII) (yield 4–15.5%)[135]:



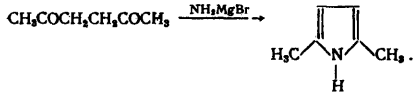
(XXVI)



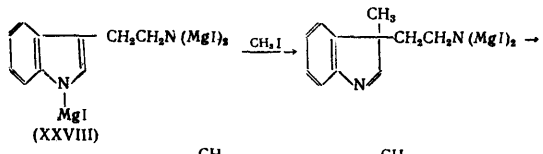
(XXVII)

where R = CH_3, C_6H_5, $C_6H_5CH_2$.

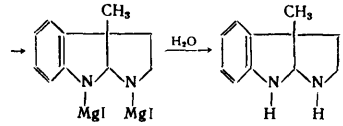
Oddo and Calderaro[3] found that reaction between aminomagnesium halide and acetonylacetone yields dimethylpyrrole:



Magnesylamines have been used for the preparation of tricyclic systems from indole derivatives. Hoshino and Tamura[23] prepared dinordeoxyeseroline (XXIX) from a trimagnesyl derivative of tryptamine (XXVIII) and methyl iodide:

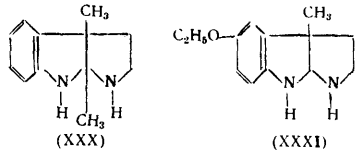


(XXVIII)



(XXIX)

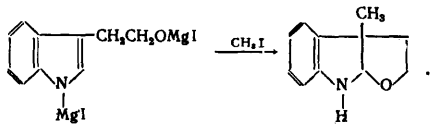
Similarly the methyl derivative of dinordeoxyeseroline (XXX)[23] was prepared from 2-methyltryptamine, and dinoreseretol (XXXI) from 5-ethoxytryptamine[136]:



(XXX) (XXXI)

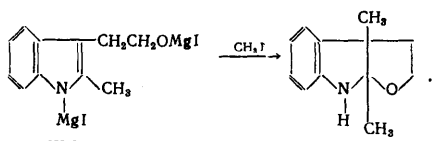
These investigations were of considerable importance for the synthesis of the fundamental cyclic structure of the alkaloid physostigmine.

Hoshino[137] also converted tryptophol (XXXII) to the furanoindoline (XXXIII):



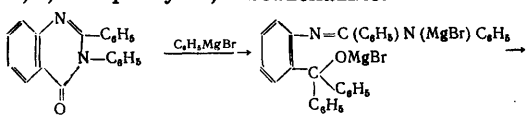
(XXXII) (XXXIII)

Very recently this reaction was employed[138] for the closure of the furan ring in 2-methyltryptophol (XXXIV):

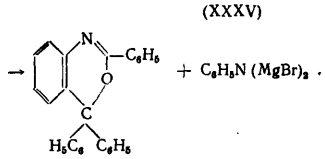


(XXXIV)

Mustafa and his coworkers[139] found that reaction of phenylmagnesium bromide with 2,3-diphenyl-4-quinazolone yields 2,6,6-triphenyl-4,5-benzoxazine:



(XXXV)

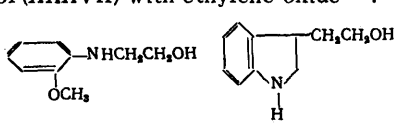


This reaction also goes *via* a stage in which a magnesylamine complex (XXXV) is formed.

8. OTHER REACTIONS

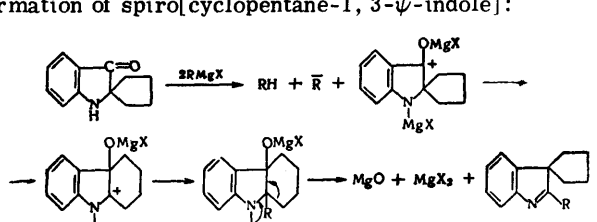
Reactions of magnesylamines with sulphur dioxide[140], hydrogen peroxide[141], ferric chloride[142], halides[9], phosphorous trichloride[143], and amides[144] have been described.

Dithiocarboxylic acids[54,140] were isolated in reactions of pyrrolyl- and indolyl-magnesium halides with carbon disulphide, the reactions with sulphonyl chloride yielding sulphones[140]. Alkene oxides react with ring opening to yield the corresponding alcohols. Thus *o*-methoxyanilinomagnesium bromide gave *o*-methoxyphenylaminoethanol (XXXVI)[145] and indolylmagnesium halide gave 2-(3′-indolyl)ethanol (XXXVII) with ethylene oxide[137]:



(XXXVI) (XXXVII)

Witkop and Patrick[146] showed that under the action of alkylmagnesium halide spiro[cyclopentane-1, 2′-ψ-indoxyl] undergoes the Wagner–Meerwein rearrangement with the formation of spiro[cyclopentane-1, 3-ψ-indole]:



It is thus evident that the rearrangement proceeds *via* a stage in which a magnesylamine is formed.

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