 © 2014 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2014v083n06ABEH004419

Azodicarboxylates: synthesis and functionalization of organic compounds †

A M Zhirov, A V Aksenov

North-Caucasus Federal University
ul. Pushkina 1a, 355029 Stavropol, Russian Federation

The data on transformations of dialkyl azodicarboxylates and their analogues involving various substrates are generalized. Nucleophilic addition and oxidation, pericyclic reactions and reactions occurring under the Mitsunobu reaction conditions are considered. Ample opportunities for application of these compounds in fine organic synthesis are shown.
The bibliography includes 245 references.

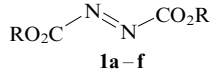
Contents

I. Introduction 502
II. Azodicarboxylates as N-electrophiles 503
III. Azodicarboxylates in pericyclic reactions 513
IV. Azodicarboxylates as oxidants 515
V. Transformations occurring under the Mitsunobu reacion conditions 517
VI. Miscellanous reactions 519

I. Introduction

Azodicarboxylates **1**, or esters of azodicarboxylic acid, are relatively stable diimines widely used in organic synthesis. The most popular representative of this class of compounds is believed to be diethyl azodicarboxylate (DEAD, **1a**); diisopropyl (**1b**), di-*tert*-butyl (**1c**), bis(2,2,2-trichloroethyl) (**1d**), dimethyl (**1e**) and dibenzyl (**1f**) azodicarboxylates are used much more rarely.

Structures 1

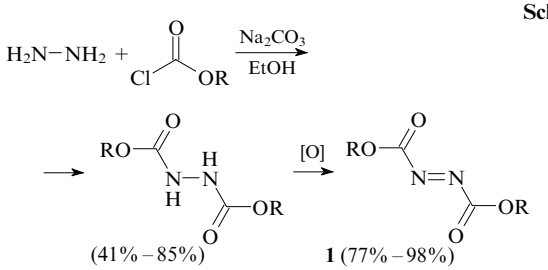


1a – f

R = Et (**a**), Pr^i (**b**), Bu^t (**c**), CH_2CCl_3 (**d**), Me (**e**), Bn (**f**)

A standard method for the synthesis of these compounds is carboalkoxylation of hydrazine followed by oxidation of the resulting hydrazodicarboxylate (Scheme 1). *N*-Bromosuccinimide,[1,2] *tert*-butyl hypochlorite,[3] iodosobenzene diacetate,[4,5] chlorine,[6] and bromine[7] can act as oxidants.

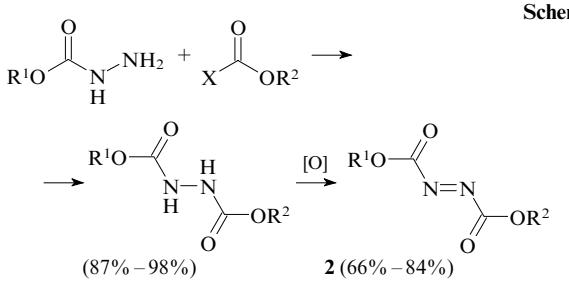
Scheme 1



R = Et, Ph, Bn, $CH_2C_6H_4Cl$-4, CH_2CCl_3, (+)-menthyl, (−)-bornyl, (−)-isobornyl, *etc*.

To obtain azodicarboxylates with different alkyl substituents in the ester groups, alkyl carbazate is used as a starting compound rather than hydrazine (Scheme 2).

Scheme 2



R^1 = Et, $(CH_2)_2SiMe_3$, n-$C_{16}H_{33}$, n-$C_{18}H_{37}$;
R^2 = Me, Et, CH_2CCl_3; X = N_3, Cl, SEt

A M Zhirov junior researcher of the Chemistry Department at the NCFU, e-mail: qereqere@gmail.com
A V Aksenov Doctor of Chemical Sciences, Professor, Head of the Chemistry Department at the NCFU, Director of the Institute of New Synthetic Methods and Materials.
Telephone: (7-918) 743 02 55, e-mail: alexaks05@rambler.ru
Current research interests: new synthetic methods in the chemistry of heterocyclic compounds.

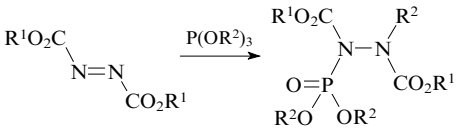
Received 8 July 2013
Uspekhi Khimii **83** (6) 502 – 522 (2014); translated by D V Aleksanyan

† Dedicated to Academician B A Trofimov on the occasion of his 75th birthday.

The intermediate unsymmetrical hydrazine is further oxidized to azo compound **2**.[8–11]

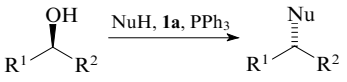
One of the first reports that mention this type of compounds was published by Diels and Fritzsche[12] in 1911. However, these reagents gained wide popularity in organic synthesis half a century later owing to the reactions of Morrison[13] (reaction with triethyl phosphite under alkali catalysis, Scheme 3) and Mitsunobu (alcohol esterification in the presence of DEAD and triphenylphosphine, Scheme 4).[14–19]

Scheme 3



R^1, R^2 = Alk

Scheme 4

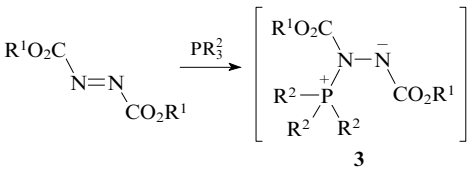


R^1, R^2 = Alk; NuH is nucleophile

The synthesis, structure and application of azodicarboxylates in organic synthesis have been surveyed.[20–26] Some aspects of reactions of these derivatives with carbonyl compounds were described in reviews,[27,28] and the addition of organometallic reagents was considered.[29]

The goal of the present review is to generalize and systematize the reactions of azodicarboxylates with various compounds. These transformations can be divided into several groups. The first group includes the reactions with nucleophiles. With rare exception, nucleophilic agents add to the N=N bond of azodicarboxylates **1** giving adducts the fate of which depends on the nucleophile nature. The adducts of azodicarboxylates with triphenylphosphine (**3**), which are the key intermediates in the Mitsunobu reaction called 'Huisgen zwitter-ions', have been most extensively studied (Scheme 5).

Scheme 5



3

In the classical Mitsunobu reaction, a quaternary phosphonium salt further reacts with carboxylic acids, but other nucleophiles can also be introduced into this process.

The second group of transformations involves pericyclic reactions such as 1,3-dipolar cycloaddition, Diels–Alder reaction and ene synthesis. The ene synthesis with azodicarboxylates does not always occur as a synchronous process; in a number of cases, the formation of zwitter-ion and biradical intermediates was proven. Since in some publications it was assumed that azodicarboxylates react with alkenes *via* a cyclic transition state, these processes will be considered as pericyclic.

Separate sections present transformations occurring under the Mitsunobu reacion conditions and oxidation of organic substrates (including functionalization of the C–H bond) under the action of azodicarboxylates, being often side reactions.

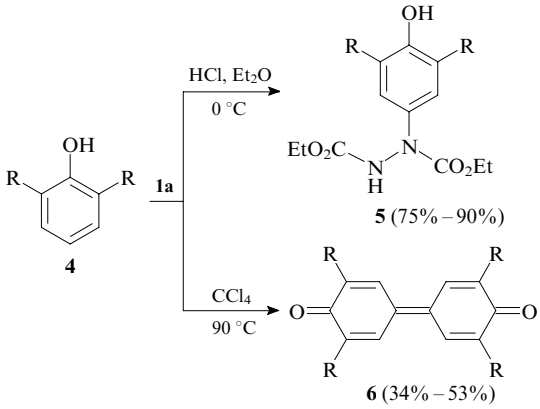
II. Azodicarboxylates as N-electrophiles

1. Formation of arylhydrazines

Currently, the formation of hydrazines from (hetero)aromatic compounds on treatment with azodicarboxylates **1** (hydrazination) has been studied in detail.

Thus, Schroeter[30] described the reaction of 2,6-disubstituted phenols with diethyl azodicarboxylate (Scheme 6). The reaction in diethyl ether saturated with hydrogen chloride gives hydrazines **5** as the major products. However, the reaction in carbon tetrachloride afforded only quinones **6**. The author assumes that dimerization of phenols **4** occurs by a radical mechanism.

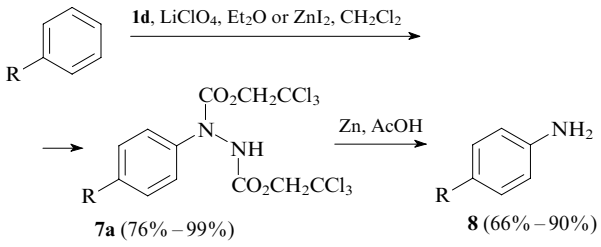
Scheme 6



R = Me, Bu^t

Leblanc and co-workers[11,31,32] developed a method for amination of arenes which is based on their hydrazination with bis(2,2,2-trichloroethyl) azodicarboxylate (**1d**) followed by reduction of the corresponding arylhydrazines with zinc. As an example, Scheme 7 shows the conversion of phenol, anisole, and *N*,*N*-dimethylaniline to hydrazines **7a** and further to amines **8**. It was demonstrated that the hydrazination can be catalyzed both by $LiClO_4$ in diethyl ether or acetone[31] and by ZnI_2 in CH_2Cl_2.[11]

Scheme 7

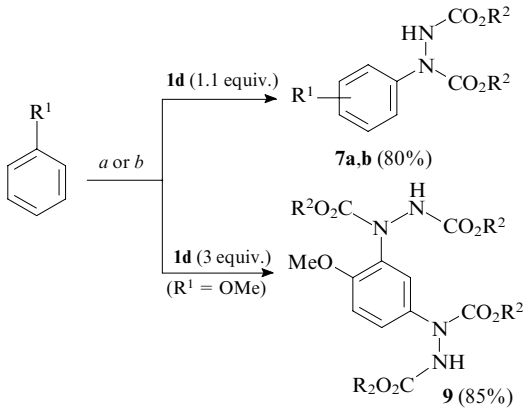


R = OH, OMe, NMe_2

The reaction is orbital symmetry-controlled. As a rule, only *para*-substituted hydrazines are formed at the first step. When Brønsted acids such as CF_3SO_3H or CF_3CO_2H are employed,[32] the reaction proceeds much faster but with lower selectivity (Scheme 8). Thus, in CF_3CO_2H in the case of phenol, along with the main *para*-isomer **7a** (R = OH, yield 52%), a considerable amount of *ortho*-isomer **7b** is

produced (R = OH, yield 48%), and in the case of anisole, there is also the product of dihydrazination **9** (1%). It should be noted that the use of three equivalents of **1d** in the reaction with anisole allows for obtaining only the product of dihydrazination **9**.

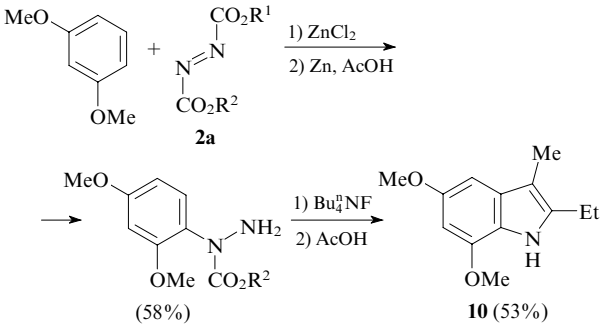
Scheme 8



(*a*) CF_3SO_3H, −78 °C, 2 h; CF_3CO_2H, 0 °C, 3 min – 3 h;
R^1 = OH, OMe; R^2 = CH_2CCl_3; isomers: *para*- (**7a**), *ortho*- (**7b**)

The same group of researchers suggested the synthesis of indole **10** from *m*-dimethoxybenzene and azo compound **2a** (Scheme 9).[11] The drawbacks of this method are low availability of the starting azodicarboxylate and relatively low yield of the indole due to the large number of steps.

Scheme 9

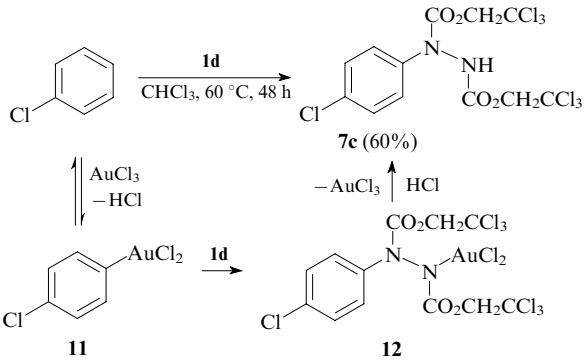


R^1 = CH_2CCl_3, R^2 = $CH_2CH_2SiMe_3$

But using $InCl_3/SiO_2$ system and microwave activation, hydrazination of arenes with reagent **1a** can be performed in several minutes, the yields of arylhydrazines being 68% – 92%.[33] Refluxing of the initial compounds in 1,2-dichloroethane leads to the corresponding arylhydrazines in lower yields and requires more time for reaction completion. Scandium triflate,[34] ruthenium chloride,[35] trifluoroacetic [36,37] and polyphosphoric [38,39] acids were also used as the catalysts of arene hydrazination.

In the presence of gold(III) chloride, chlorobenzene and azodicarboxylate **1d** react to give hydrazine **7c** in a moderate yield (Scheme 10).[40] The authors assume that the reaction proceeds through the formation of organogold intermediates **11** and **12**.

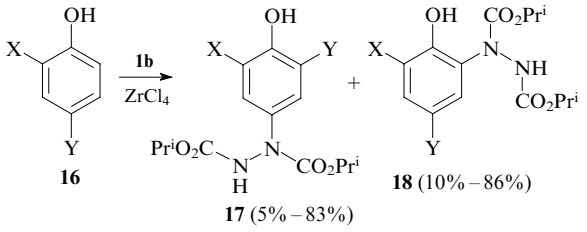
Scheme 10



An efficient catalyst for the addition of azo compounds **13** to arenes is $ZrCl_4$ (Scheme 11).[41] The yields of regioisomeric hydrazines **14a**,**b** are rather high. Whereas in the case of *m*-xylene, the yields of products **14a**,**b** (Ar = 2,4-$Me_2C_6H_3$) are almost equal, the reaction with toluene affords predominantly hydrazine **14a** (Ar = 4-MeC_6H_4). It should be noted that this catalyst was also used for intramolecular cyclization of compounds **13** into benzimidazole derivatives **15** (the substituent position in the initial aniline is indicated).

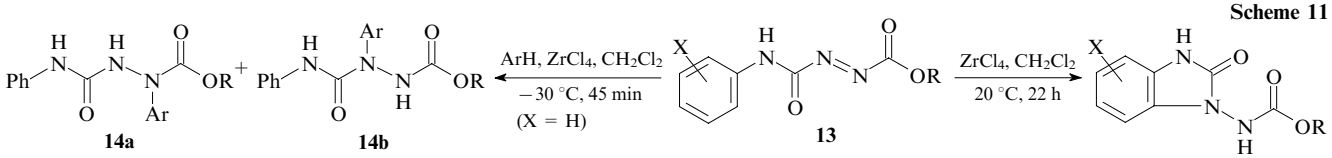
Unexpectedly it was found that the hydrazination of halophenols **16** with azodicarboxylate **1b** results in the migration of the halogen atom and formation of products **17** (Scheme 12).[42,43] Note that in the absence of a hydrazination agent, this process was not detected. Furthermore, the products of hydrazination at position 2 of the halophenol do not rearrange under reaction conditions. The migration of the halogen atom upon hydrazination proceeds most readily in 2,4-dihalophenols; 4-halophenols and azodicarboxylates mainly form the products of addition at position 2 (compounds **18**) with insignificant amount of rearrangement products **17** (see Scheme 12). However, this reaction is very sensitive to the catalyst nature. Thus, no reaction took place upon replacement of zirconium chloride by the fluoride; the application of zirconium bromide resulted in bromoarenes and reduced azo compounds **17** and **18**.[44]

Scheme 12



X, Y = H, F, Cl, Br, I

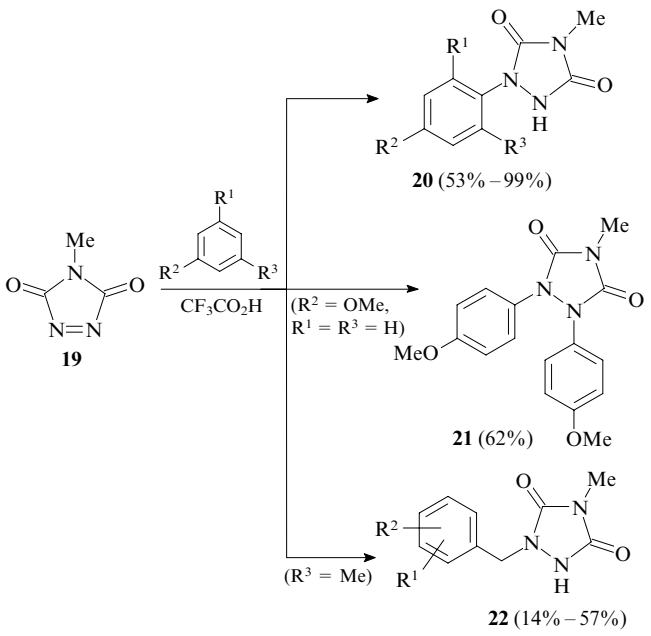
Scheme 11



X = H, 4-Me, 4-OMe, 4-F, 3-Cl; R = Me, Et, Bu^t; ArH = PhMe, 1,3-$Me_2C_6H_4$

The addition of formal imide of azodicarboxylic acid — 4-methyl-1,2,4-triazole-3,5-dione (**19**) — to arenes in the presence of trifluoroacetic acid serves as the convenient method for the synthesis of 1-arylurazoles **20** (Scheme 13).[45] Interestingly, in the reaction with anisole, the major product is 1,2-diarylurazole **21**. This process is carried out under irradiation with visible light.[46] However, if the initial arene contains the methyl group, then 1-benzylurazole **22** is formed along with 1-arylurazole. The authors suggest that the process occurs through the formation of radical ion pairs, which is in agreement with the experimental and computation data.

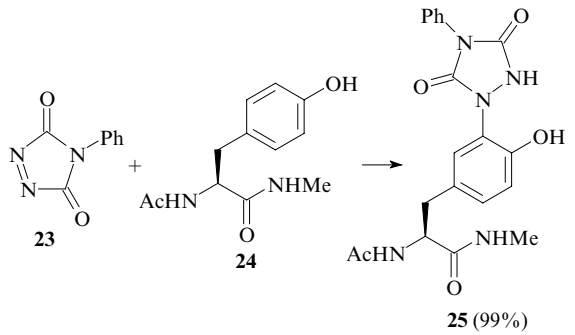
Scheme 13



R^1 = H, Me, OMe; R^2 = Me, OMe; R^3 = H, Me, OMe, Ac, CO_2Me

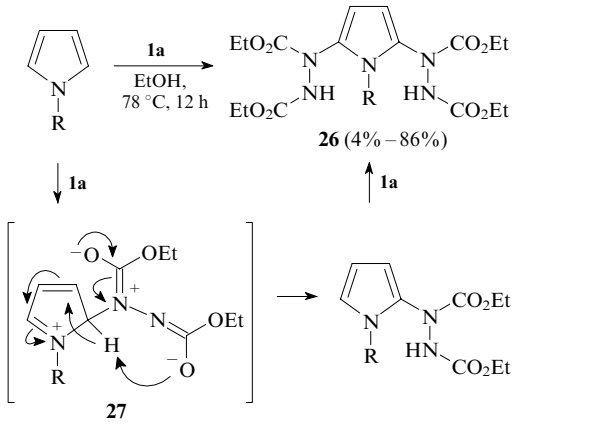
The addition of a phenyl analogue of azo compound **19** — 4-phenyl-1,2,4-triazole-3,5-dione (**23**) — to the methylamide of *N*-acetyltyrosine (**24**) occurs under mild conditions and can be used for peptide labelling (Scheme 14).[47, 48] The reaction proceeds in a phosphate buffer at room temperature over several minutes. The advantages of this method are high chemoselectivity and stability of the resulting adduct **25** with respect to pH and high temperature.

Scheme 14



Pyrroles readily react with DEAD at room temperature in the absence of a catalyst in a mixture of diethyl ether and n-pentane giving products of hydrazination at the α-position. If a substrate contains substituents at positions 2 and 5, the hydrazination involves the free β-positions.[49] N-Substituted pyrroles give the 2,5-dihydrazination products **26** (Scheme 15).[50]

Scheme 15

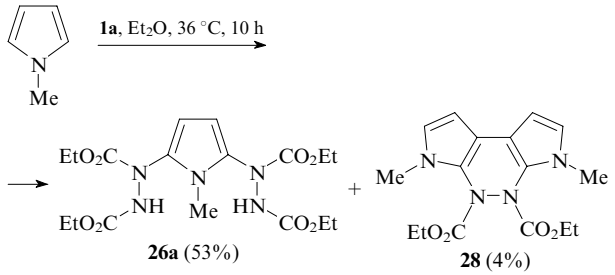


R = Alk, Ar

The authors assume that the process occurs as the Michael reaction *via* formation of zwitter-ion intermediate **27**. Then, in the case of an aprotic solvent, the hydrogen atom from the α-position migrates to the oxygen atom, resulting in a six-membered transition state. Apparently, the solvation or protonation involving the solvent can stabilize intermediate **27** and increase the amount of the target product. Indeed, replacement of diethyl ether by ethanol results in higher yields of compound **26** in the case of *N*-alkylpyrroles.

It should be noted that the reaction with methylpyrrole in diethyl ether affords by-product **28** along with the major dihydrazination product **26a**. The by-product results from [2 + 2 + 2]-cycloaddition (Scheme 16).[51]

Scheme 16

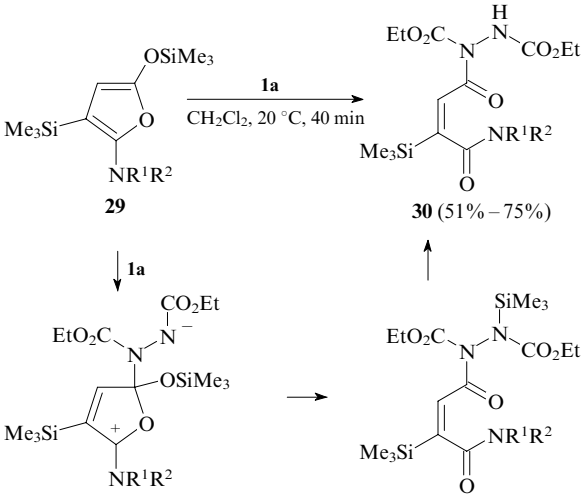


Heating of aminopyrimidines with DEAD leads to hydrazination products at position 5. The reaction is likely to proceed as a synchronous process.[52]

The reaction of compound **1a** with furans **29** results in cleavage of the furan ring (Scheme 17).[53] According to the authors' suggestion, the reaction proceeds by electrophilic hydrazination mechanism followed by opening of the five-membered ring and formation of products **30**.

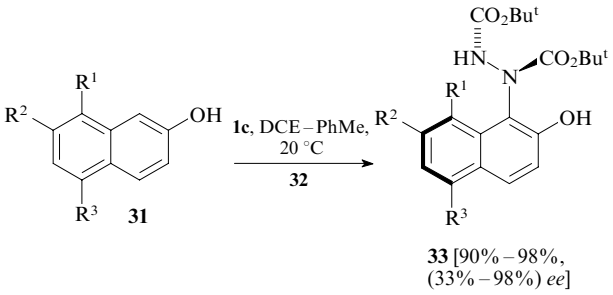
On treatment with di-*tert*-butyl azodicarboxylate (**1c**) in the presence of asymmetric base **32**, substituted 2-naphthols **31** give chiral compounds **33** with high enantiomeric excess (*ee*) (Schemes 18 and 19).[54] It is noteworthy that quinine alkaloid **32** used as the catalyst can also add a molecule of azo compound **1c** to form diastereomeric hydrazines **34a** and **34b** (3.5 : 1 ratio). Interestingly, the base modified in this manner is not only not inferior to its precursor in the

Scheme 17



R^1 = Me: R^2 = Bn, CH(Me)Ph; R^1-R^2 = $(CH_2)_5$, $(CH_2)_2O(CH_2)_2$

Scheme 18



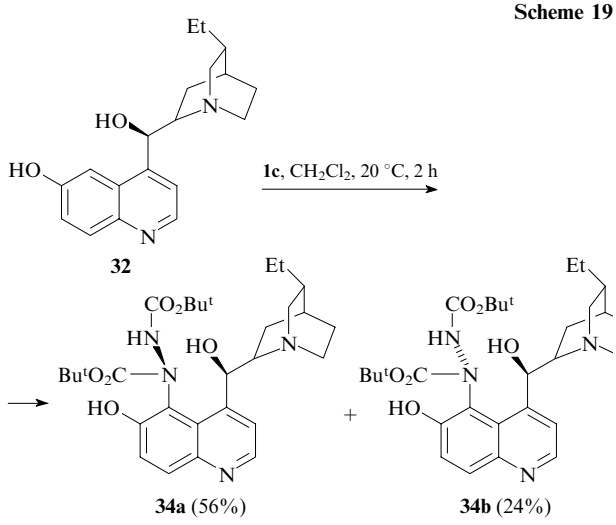
R^1 = H, NH_2, NHMe, NHC_5H_{11}-n, NHBn; R^2, R^3 = H, Br;
DCE is dichloroethane

catalytic activity but in a number of cases, even demonstrates better results.

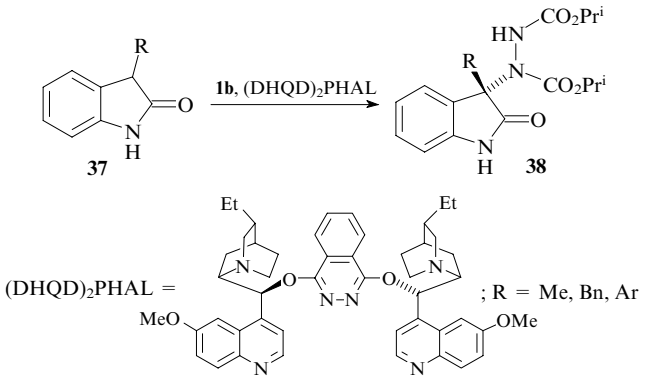
The reaction of 2,2′-biindoles **35** with DEAD yields compounds **36** being the formal [4 + 2]-cycloaddition products.[55] However, the authors postulate a stepwise mechanism of their formation (Scheme 20).

The hydrazination of 2-oxindoles **37** with azodicarboxylate **1b** in the presence of asymmetric catalyst $(DHQD)_2PHAL$ gives the corresponding chiral arylhydrazines **38** (Scheme 21).[56, 57] This reaction was carried out independently by two research groups. In one case,[56] the yields of products **38** ranged from 54% to 100% with 63%–99% *ee*, while in the other case,[57] the yields were 87%–98% and *ee* values were 76%–99%.

Scheme 19

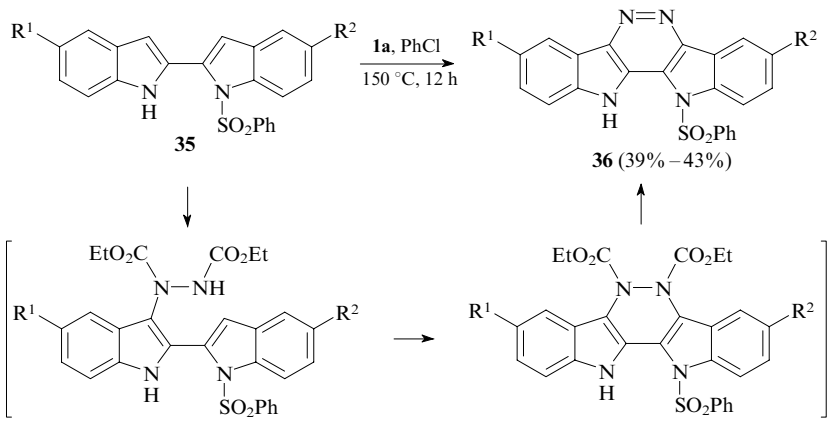


Scheme 21



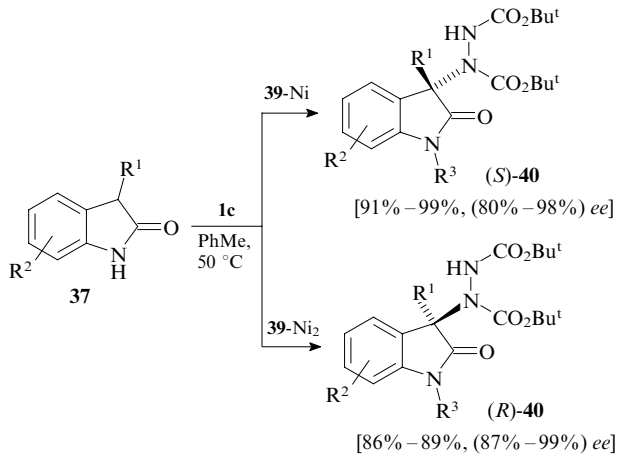
Using nickel Schiff base complexes **39**, it is possible to control the stereochemical outcome of the reaction of 2-oxindoles **37** and azo compound **1c** (Scheme 22). The mononuclear complexes afford the *S*-isomers of **40** while the binuclear complexes lead to the *R*-isomers.[58]

Scheme 20

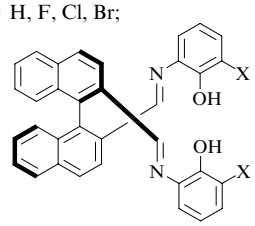


R^1 = Cl, Me; R^2 = H, Cl

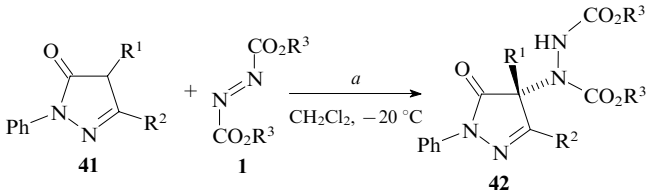
Scheme 22



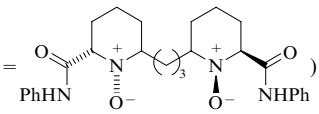
R^1 = Me, Bn, All, (*E*)-cinnamyl, CH_2CO_2Me, CH_2CN;
R^2 = H, F, Cl, Br;

39 =  (X = NH, Bu^t, OH, OMe)

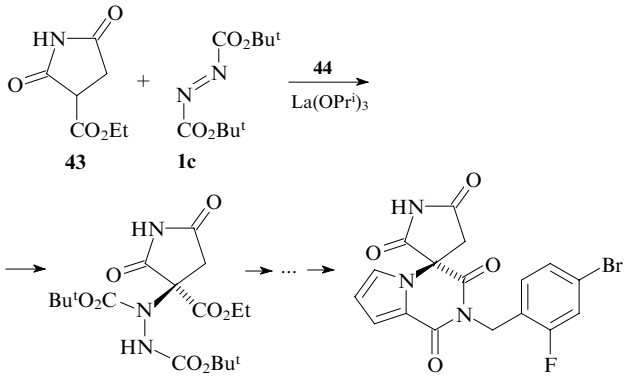
Scheme 23

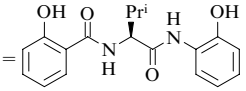


R^1, R^2 = Me, Et, Pr^n, Bn, Ph; R^3 = Et, Pr^i, Bu^t, Bn;

(*a*) $LGd(OTf)_3$ (L = ) or quinine

Scheme 24



44 = 

On treatment with **1** upon catalysis with a chiral gadolinium trifluoromethylsulfonate (triflate) complex, pyrazolones **41** are converted to asymmetric hydrazines **42** in 85%–99% yields and 90%–97% *ee*.[59] Upon application of quinine as an optical inductor, both the yields of products **42** and the enantiomeric excess values decrease (to 55%–85% and 82%–84%, respectively) (Scheme 23).[60]

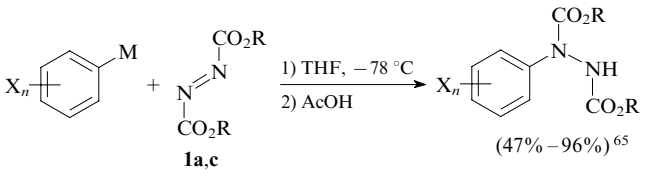
The reaction of substituted succinimide **43** and di-*tert*-butyl azodicarboxylate (**1c**) in the presence of chiral catalyst **44** leads to hydrazine **45** in almost quantitative yield. Then compound **45** was used to obtain the AS-3201 agent (Ranirestat), which is an aldose reductase inhibitor promising for treating diabetic neuropathy (Scheme 24).[61, 62]

2-(Methoxycarbonylmethylidene)-5-diethylaminodihydropyrrol-3-one readily reacts with DEAD at room temperature to give the monoaddition product.[63] Various imidazoles also give monoaddition products with azodicarboxylates, but the reaction mixture must be heated to 100–110 °C to make the process efficient.[64]

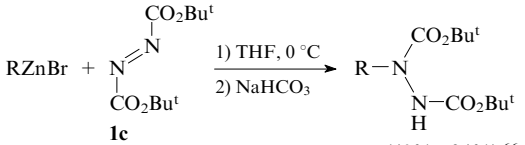
2. Reactions with organometallic compounds

The addition of organometallic derivatives to azodicarboxylates occurs vigorously and often requires cooling to rather low temperatures. Thus, various substituted hydrazines were obtained from the corresponding azodicarboxylate and organolithium, -magnesium and -zinc compounds.[29, 65–68] The examples of these reactions are presented in Scheme 25.

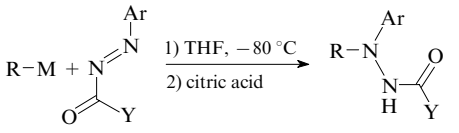
Scheme 25



M = Li, MgBr; X_n = H, 2-CF_3, 4-MeS, 4-(n-C_5H_{11})O, 3,4-$(MeO)_2$;
R = Et, Bu^t



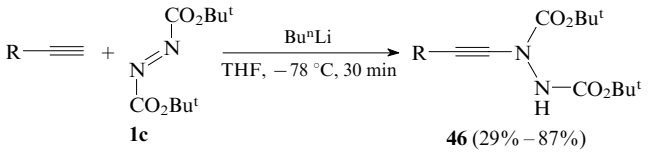
R = Alk, Ar, Het



Y = OBu^t, Me; R = Alk, Ar; M = Li, ZnCl, MgCl

The *in situ* generated lithium acetylides add to azodicarboxylates (*e.g.*, reagent **1c**), giving the corresponding ynehydrzaines **46** (Scheme 26).[69]

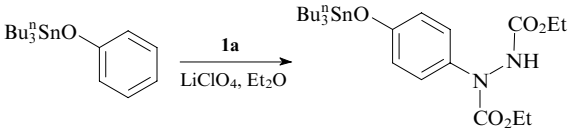
Scheme 26



R = H, Alk, Ar, $SiMe_3$

Tri-n-butyltin phenoxide readily reacts with compound **1a** in a diethyl ether solution of lithium perchlorate affording organotin hydrazine **47** (Scheme 27).[70–73]

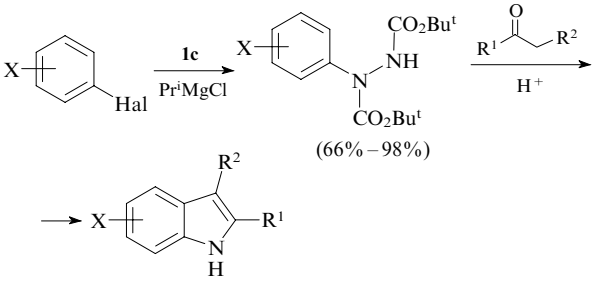
Scheme 27



47 (100%)

The addition of organometallic compounds to azodicarboxylates was used in the Fischer synthesis of indoles **48** (Scheme 28).[74, 75] An extensive series of substituted indoles were obtained in this way in acceptable yields.

Scheme 28

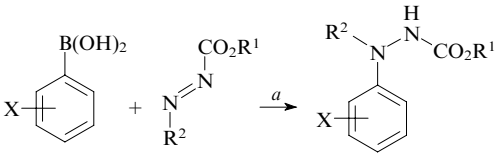


48 (66%–100%)

R^1, R^2 = Me, Ph, CO_2H, CO_2Et;
X = F, Cl, Br, TsO, CO_2Me, Me, MeO, NO_2;
Ts is *p*-toluenesulfonyl (tosyl)

Arylboronic acids can act as analogues of organometallic compounds. The addition of symmetrical and unsymmetrical azodicarboxylates ($R^2 = CO_2Bu^t$) as well as aryl azocarboxylates **49** (R^2 = Ar) to them, resulting in arylhydrazines **50**, is catalyzed both by copper acetate (yields 18%–100%;[76] or 5%–99%;[77]) and by palladium complex (yields 40%–99%)[78] (Scheme 29).

Scheme 29



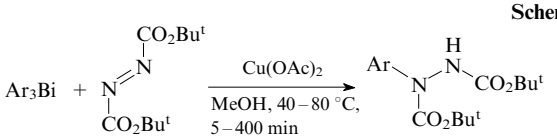
1c, **2**, **49** **50**

X = H, Me, Bu^t, Ph, CF_3, F, Cl, Br, I, OH, OMe, NO_2, NMe_2, CHO, Ac, CO_2Et, CN; R^1 = Et, Pr^i, Bu^t, Bn; $R^2 = CO_2Bu^t$, Ph, 4-$NO_2C_6H_4$, 2,4-$(NO_2)_2C_6H_3$;
(*a*) $Cu(OAc)_2$ or [(bathocuproine)Pd(dba)];
bathocuproine is 2,6-dimethyl-4,7-diphenyl-1,10-phenanthroline, dba is dibenzylideneacetone

Copper salts are also used as catalysts for the addition of azo compounds to triarylbismuth (Scheme 30).[79]

The one-pot reaction of pyridine, alkyl- or phenyllitium and azo derivative **1c** affords hydrazines **51** in 28%–73% yields (Scheme 31).[80] The organolithium compound and azodicarboxylate sequentially add to the pyridine molecule, then the aromatization under acid catalysis takes place.

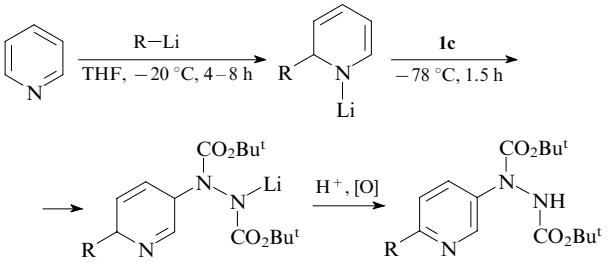
Scheme 30



1c (15%–84%)

Ar is naphthyl, *o*-tolyl

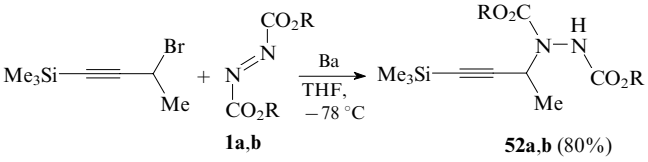
Scheme 31



R = Alk, Ph **51** (28%–73%)

Propargylhydrazines **52a**,**b** were obtained by the reaction of azo compounds **1a**,**b** with *in situ* generated 1-trimethylsilylbut-1-yne-3-barium bromide (Scheme 32).[81]

Scheme 32



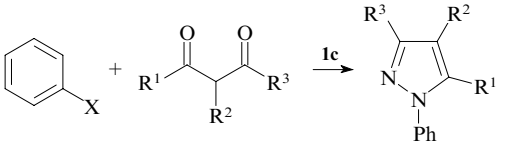
1a,**b** **52a**,**b** (80%)

R = Et (**a**), Pr^i (**b**)

Analogous hydrazines are formed from propargyl alcohol ethers, reagent **1c**, $Ti(OPr^i)_4$ and Pr^iMgCl in a one-pot process.[82]

The same method was used to synthesize *N*-arylpyrazoles **53** starting from lithium or magnesium phenyl derivative, 1,3-dicarbonyl compound and azodicarboxylate **1c** (Scheme 33).[83]

Scheme 33

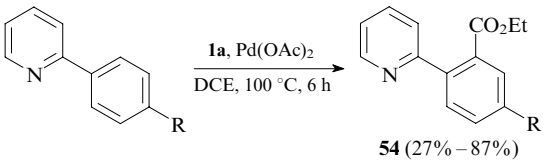


53 (22%–75%)

X = Li, MgCl; R^1, R^2, R^3 = H, Me, Cl

An unusual reaction of DEAD with organometallic compounds formed upon cyclopalladation of 2-arylpyridines was reported (Scheme 34).[84] This process results in

Scheme 34



54 (27%–87%)

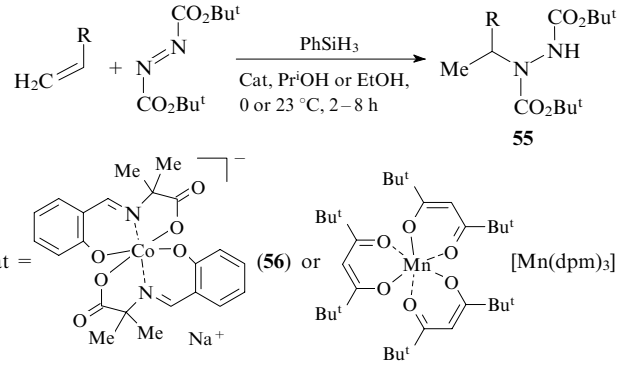
R = H, Me, CHO, MeO

carboethoxylation products **54**. The authors assume that the reaction proceeds by a radical mechanism.

3. Addition of azodicarboxylates to alkenes

The addition of reagent **1c** to various alkenes catalyzed by cobalt or manganese complexes in the presence of phenylsilane has been reported (Scheme 35).[85–87] Upon catalysis by $Mn(dmp)_3$ (dpm is 2,2,6,6-tetramethylheptane-3,5-dionate), the yields of products **55** are 51%–98%, while in the case of cobalt complex **56** as the catalyst, the yields are considerably lower (10%–74%).[85]

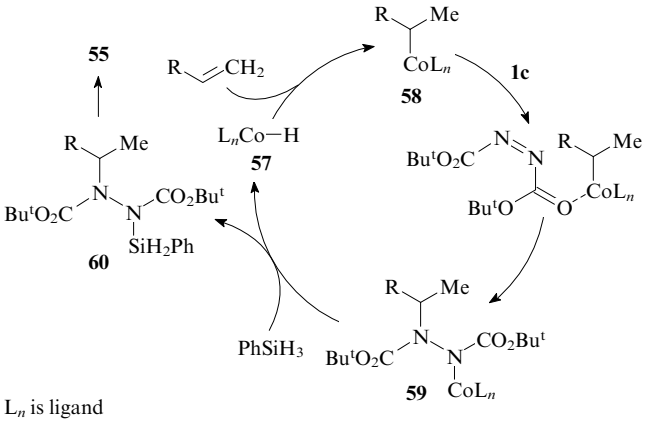
Scheme 35



R = Ph, $(CH_2)_2Ph$, CH_2OH, CH_2OBn, $(CH_2)_2Bz$, $CH(OMe)_2$

A proposed catalytic cycle of this transformation is presented by the example of cobalt catalyst (Scheme 36).[86] Cobalt complex **56** reacts with phenylsilane to generate hydrido cobalt intermediate **57**, which adds to the alkene double bond to give organocobalt compound **58**. Then complex **58** adds to the N=N bond of **1c** yielding hydrazine cobalt derivative **59**. The subsequent reaction with phenylsilane proceeds as σ-bond metathesis, which results in hydrazination product **60** and regeneration of intermediate **57**.

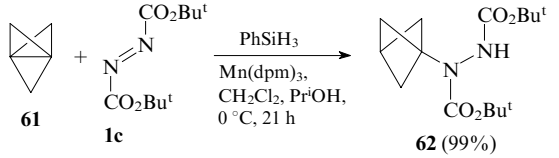
Scheme 36



L_n is ligand

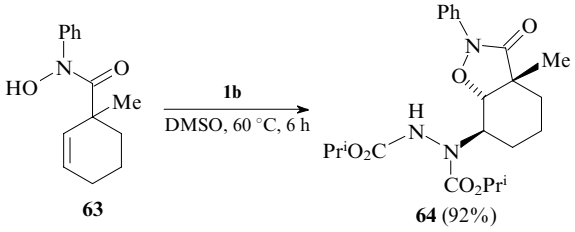
Using a similar procedure, hydrazine **62** was synthesized from [1.1.1]propellane **61** in almost quantitative yield (Scheme 37).[88]

Scheme 37



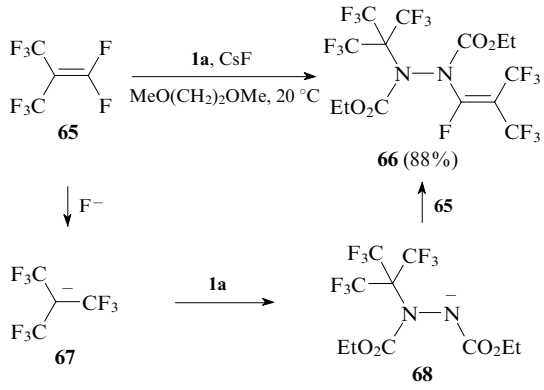
The reaction of hydroxamic acid **63** with azodicarboxylate **1b** affords bicyclic compound **64** with a high stereoselectivity [diastereomeric ratio (*dr*) > 95 : 5] and in a high yield (Scheme 38).[89,90] The authors suggest that the reaction follows a radical mechanism.

Scheme 38



Diethyl azodicarboxylate (**1a**) reacts with perflurorisobutene **65** in the presence of caesium fluoride yielding enehydrazine **66** (Scheme 39).[91] Apparently, in this case, the reaction proceeds through the formation of anions **67** and **68**.

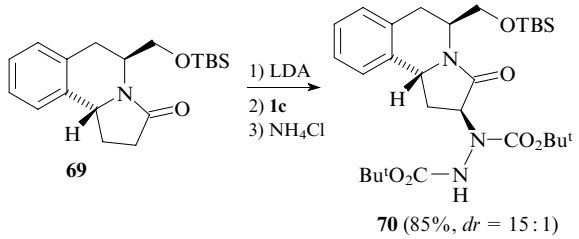
Scheme 39



4. Hydrazination of compounds with activated C–H bond

The functionalization of carbonyl compounds at the α-position is a principal method for the synthesis of practically important compounds such as α-amino acids, α-amino ketones and α-amino aldehydes.[27,28,92,93] A particular place among the reactants used for this purpose is held by azodicarboxylates, since their addition to carbonyl compounds occurs readily[94–98] and is easily subjected to stereocontrol. Several aapproaches to the formation of an asymmetric centre in the α-position of the carbonyl compound can be highlighted. The first approach consists in the stereocontrol by means of the substrate.[99–104] An example of this sterecontrol is the reaction of optically active pyrroloisoquinoline enolate **69** with di-*tert*-butyl azodicarboxylate, resulting in hydrazine **70** with good stereoselectivity (Scheme 40).[105]

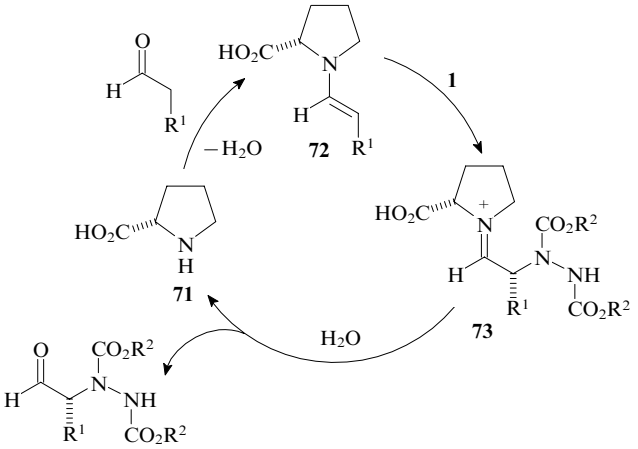
Scheme 40



TBS = $SiBu^tMe_2$; LDA is lithium diisopropylamide

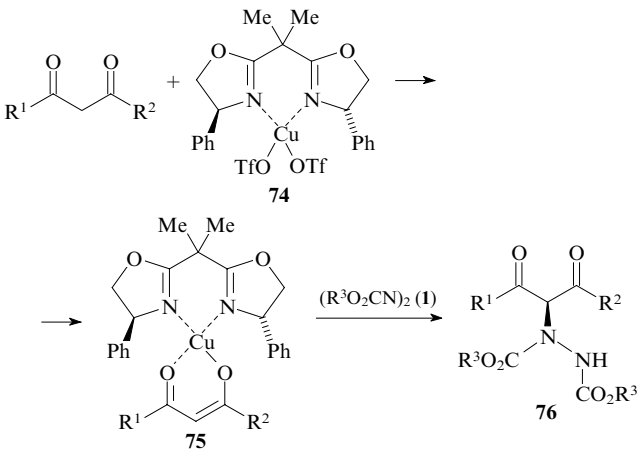
The second approach implies the use of a chiral amino acid, *e.g.*, L-proline (**71**), as a catalyst. L-Proline forms asymmetric enamine **72** with the carbonyl compound, to which azodicarboxylate adds to give cation **73** (Scheme 41). This method was developed independently by Jorgensen and co-workers[106] and List.[107] Other amino acids,[108–121] cyclic aminals,[122] guanidine[123–125] and urea[126–129] derivatives can also act as chiral catalysts. The high efficiency in this reaction was demonstrated also by quinoline alkaloids.[130–137]

Scheme 41



The third approach is based on the application of metal complexes with chiral ligands as catalysts. The carbonyl compound forms an enolate complex with the metal and the ligand to which the azo compound adds stereoselectively. An example of this reaction is shown in Scheme 42.[138] The diketone substitutes the TfO groups in bis(isoxazoline) copper complex **74**, leading to intermediate **75**. The latter reacts with the azodicarboxylate giving chiral hydrazine **76**. For coordination of the carbonyl compound and asymmetric ligand, copper,[139–143] palladium,[144–146] magnesium,[147] nickel,[148] ruthenium, iridium,[149] lanthanum,[150] and silver[151] ions are used.

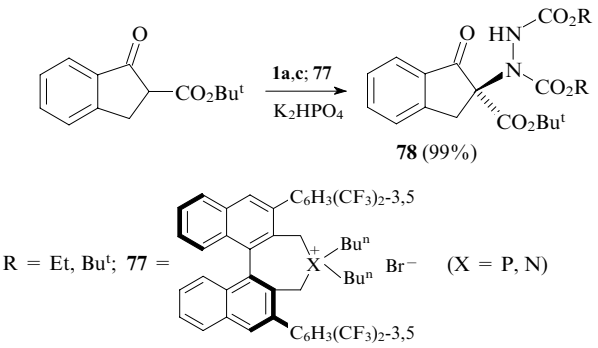
Scheme 42



R^1 = Me, Et, Ph, Pr^i, Bn; R^2 = OEt, OBu^t; R^3 = Alk

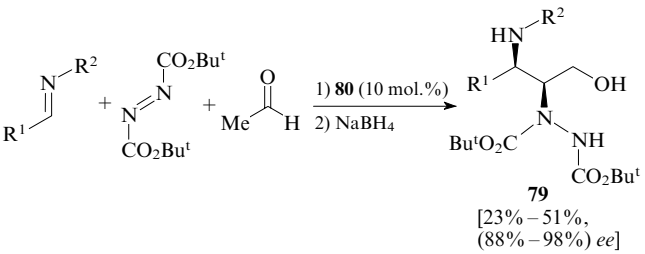
The fourth method for asymmetric hydrazination of 1,3-dicarbonyl compounds is the use of chiral phase transfer catalysts based on quaternary phosphonium[152,153] or ammonium salts (Scheme 43).[154] This method afforded compounds **78** in quantitative yield (99%) and with high diastereoselectivity (*ee* was 91% for X = P and 95% for X = N) from *tert*-butyl-1-oxoindane-2-carboxylate in the presence of salts **77**.

Scheme 43

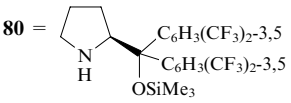


Based on the above-mentioned methods for hydrazination of carbonyl compounds with azodicarboxylates, a series of tandem transformations was developed which are considered below. For example, the hydrazination of aldehydes can be combined with the Mannich reaction as a one-pot process; this was used to prepare compounds **79** (Scheme 44).[155] Chiral derivative of pyrrolidine **80** was used as a catalyst.

Scheme 44

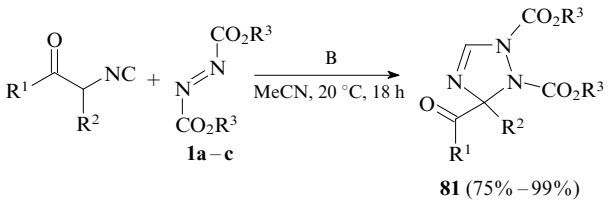


R^1 = Ph, 4-MeC_6H_4, 4-ClC_6H_4, 3-ClC_6H_4, 4-FC_6H_4, 3-$MeOC_6H_4$, 2-$MeOC_6H_4$, 2-naphthyl; R^2 = Bz, CO_2Bn, CO_2Bu^t;



1,2,4-Triazolines **81** are formed from α-isocyanoesters and azo compounds **1a–c** in the presence of a base — triethylamine, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD). The process occurs as hydrazination followed by ring closure (Scheme 45).[156]

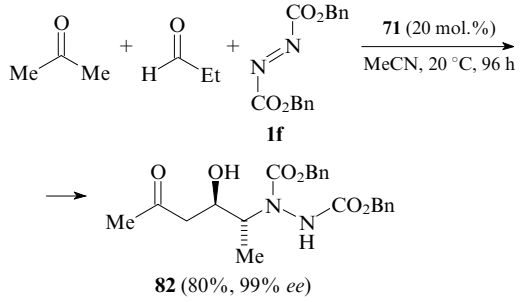
Scheme 45



R^1 = OAlk, $NAlk_2$; R^2 = Alk, Ar; R^3 = Et, Pr^i, Bu^t;
B = Et_3N, DBU, TBD

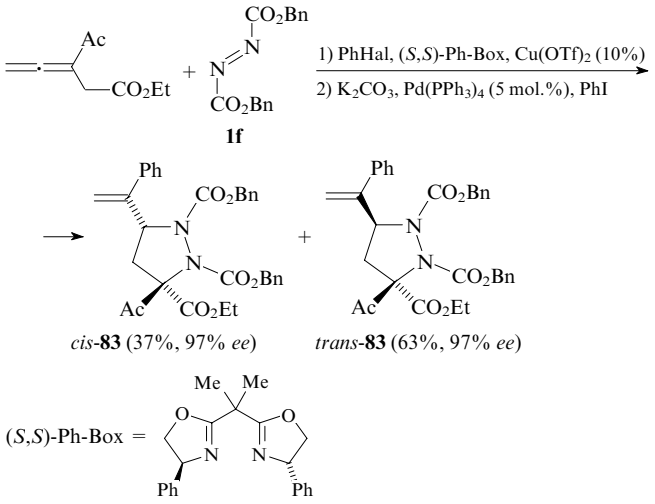
The reaction of acetone, propionic aldehyde and azodicarboxylate catalyzed by L-proline (**71**) leads to hydrazine **82** (Scheme 46).[157] The ratio of *anti*- and *syn*-isomers of the product is 56 : 44.

Scheme 46



Optically active pyrazolidines *cis*-**83** and *trans*-**83** were obtained using Cu- and Pd-catalyzed tandem transformations of the corresponding allene, halobenzene and dibenzyl azodicarboxylate (Scheme 47). It should be noted that the

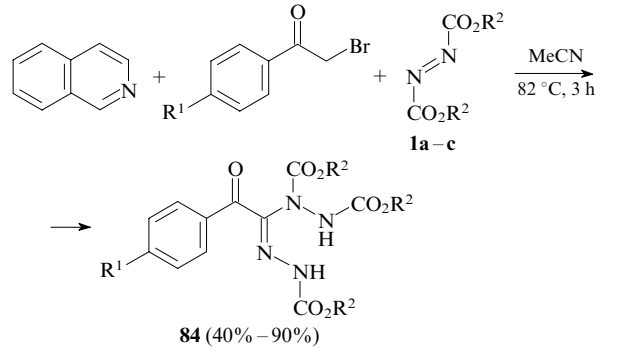
Scheme 47



ratio of diastereomeric products depends on the structure of the chiral ligand used at the first step. Thus, upon application of *S*,*S*-stereoisomer of 2,2′-bis[(*S*)-4-phenyl-4,5-dihydrooxazol-2-yl]propane (Ph-Box), the main product is pyrazolidine *cis*-**83**, whereas in the case of (*R*,*R*)-Ph-Box, the *trans*-isomer is formed predominantly.[158, 159]

The *in situ* generated phenacyl salts of isoquinoline react with two equivalents of azodicarboxylate **1** to give compounds **84** in 40%–90% yields (Scheme 48).[160]

Scheme 48

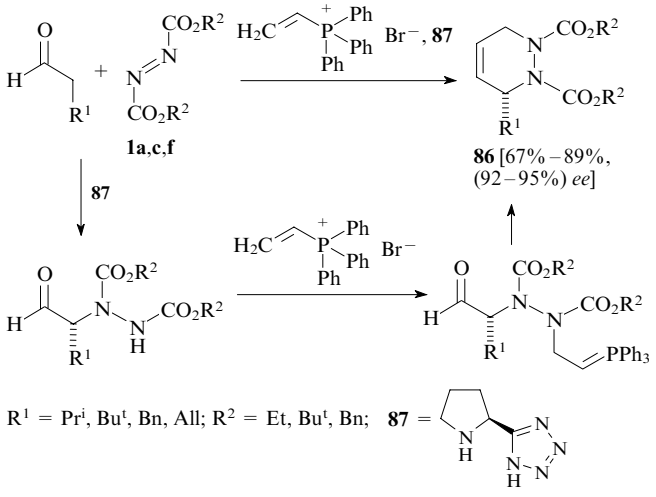


R^1 = H, Cl, Br, OMe, NO_2; R^2 = Et, Pr^i, Bu^t

Propargylhydrazines **85** were synthesized from aldehydes *via* a one-pot method: hydrazination followed by the Seyferth–Gilbert alkynylation.[161] Proline was used as a catalyst (**71**); the putative mechanism of transformation is presented in Scheme 49.

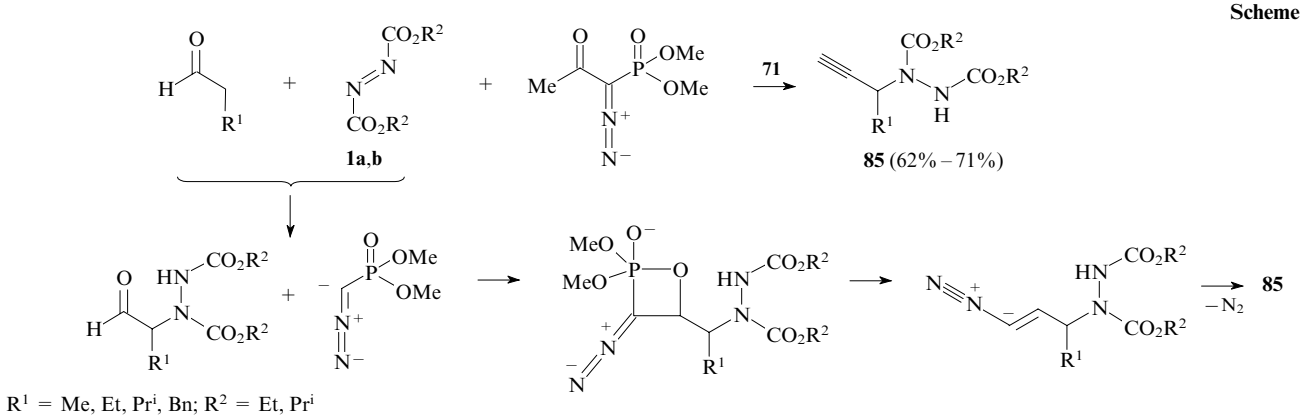
Chiral 1,2,3,6-tetrahydropyridazines **86** are formed upon the reaction of aliphatic aldehydes with azodicarboxylates **1** in the presence of vinyltriphenylphosphonium salt and asymmetric inductor **87** (Scheme 50). Probably, the

Scheme 50



R^1 = Pr^i, Bu^t, Bn, All; R^2 = Et, Bu^t, Bn; **87** =

Scheme 49

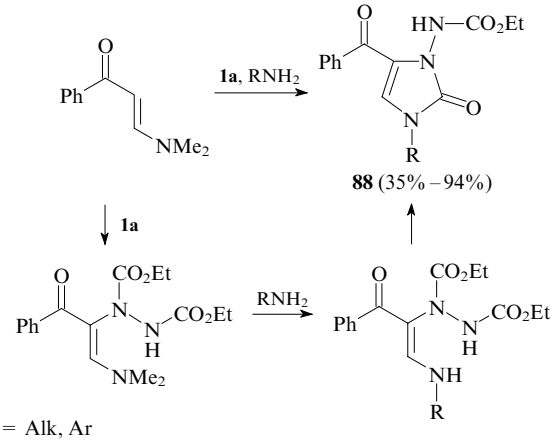


R^1 = Me, Et, Pr^i, Bn; R^2 = Et, Pr^i

reaction proceeds through successive stages of hydrazination, addition of the vinylphosphonium salt and Wittig cyclization.[162]

The tandem reaction of 3-dimethylamino-1-phenylpropenone, DEAD and primary aliphatic or aromatic amine leads to dihydroimidazolone **88** (Scheme 51).[163] The addition of azodicarboxylate **1a** to the double bond of the enamine is likely to occur first, being followed by transamination and cyclization.

Scheme 51



R = Alk, Ar

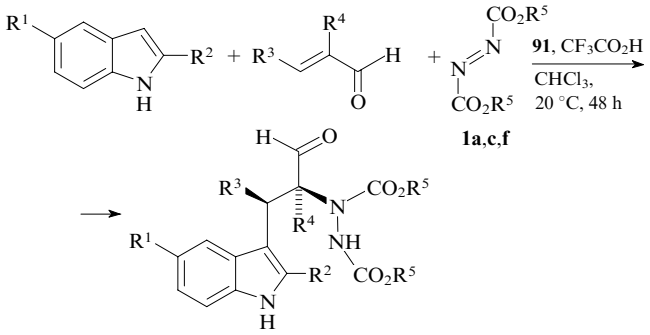
The base-catalyzed tandem transformation of unsaturated aldehyde **89**, reagent **1a** and benzaldoxime affords alcohol **90** (Scheme 52).[164] The process occurs with good stereoselectivity in the presence of a chiral amine — substituted pyrrolidine **80**.

A series of optically active 3-hydrazinoethylindoles **92** were synthesized by the reaction of indoles, unsaturated aldehydes and azo compounds **1** upon catalysis by quinine derivatives **91** (Scheme 53).[165]

If thiols are used as nucleophiles instead of indoles, the reaction leads to chiral hydrazines **93** (Scheme 54).[165]

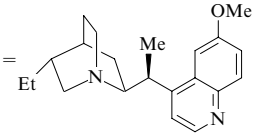
Azodicarboxylates can function as the carbonyl component in the Baylis–Hillman reaction and add to α,β-unsaturated derivatives in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) giving enehydrazines **94** (Scheme 55).[166, 167]

Scheme 53

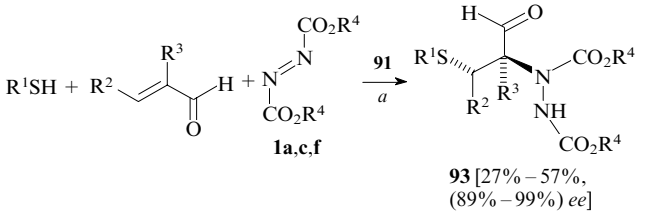


R^1 = H, Me, Cl, MeO; R^2 = H, Me; R^3 = Et, Pr^n; R^4 = Me, Et; R^5 = Et, Bu^t, Bn;

91 =



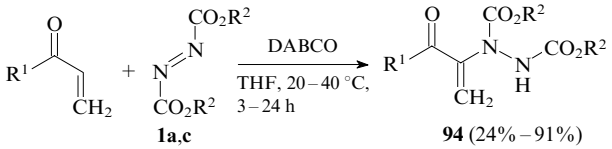
Scheme 54



R^1 = Bu^t, Bn; R^2 = Me, Et, Ph; R^3 = Et, Bu^n, Ph; R^4 = Et, Bu^t, Bn

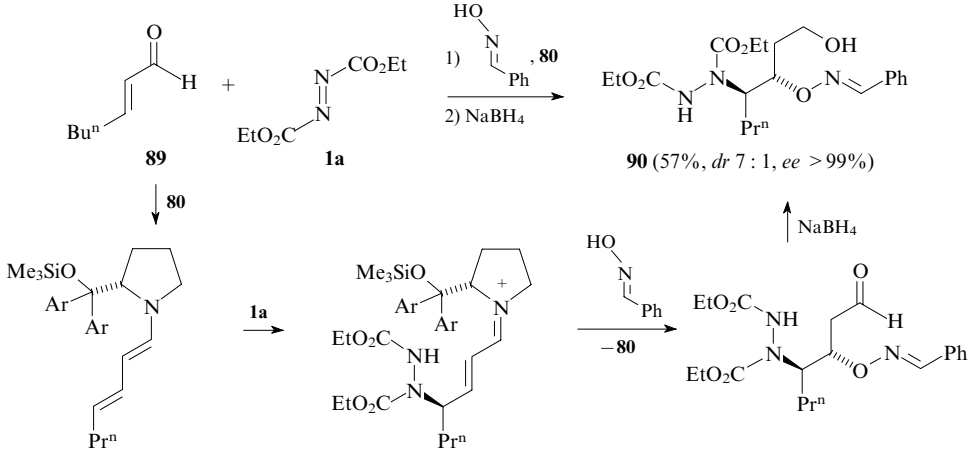
(*a*) CF_3CO_2H, $CHCl_3$, −20 → 0 °C, 48–65 h

Scheme 55



R^1 = Me, Et, n-C_6H_{13}, n-C_7H_{15}, OMe, CH═CHPh; R^2 = Et, Bu^t

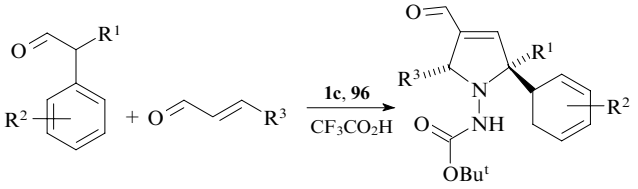
Scheme 52



Ar = 3,5-$(CF_3)_2C_6H_3$

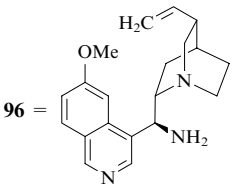
The one-pot reaction of di-*tert*-butyl azodicarboxylate (**1c**) with aryl-substituted acetaldehydes and acrolein or crotonaldehyde afforded pyrrolines **95** (Scheme 56).[168] Quinine alkaloid **96** served as the catalyst, while trifluoroacetic acid was the solvent.

Scheme 56



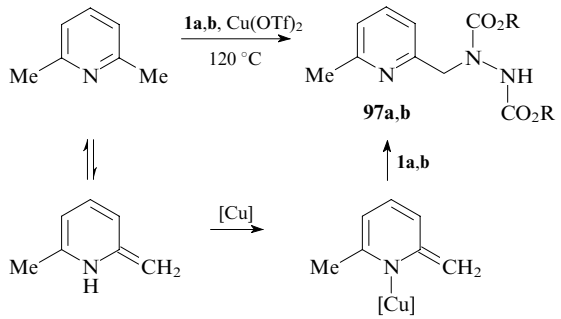
95 [26%–83%, (30%–98%) *ee*]

R^1 = Me, Et, Pr^n; R^2 = H, 2-Me, 3-Me, 4-Me, 4-F, 4-Br; R^3 = H, Me;



It should be noted that azodicarboxylates can add to azaarenes with activated methyl hydrogen atoms as they add to carbonyl compounds (Scheme 57).[169] Apparently, this transformation proceeds through the formation of a enamide form and is facilitated by an increase in the acidity of methylene protons under the action of copper triflate.[169] An example of this reaction can be the formation of pyridyl-substituted hydrazines **97a**,**b** from 2,6-lutidine.

Scheme 57

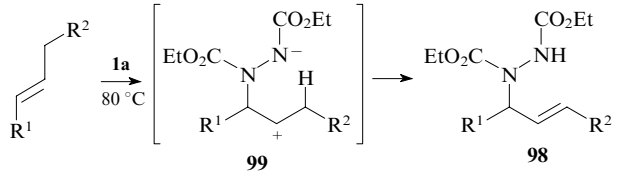


R = Et (**a**, yield 75%), Pr^i (**b**, 74%)

III. Azodicarboxylates in pericyclic reactions

The reaction of diethyl azodicarboxylate with alkenes giving ene reaction products **98** has been reported.[170] Acyclic alkenes add the azo deriavtives, initially resulting in zwitter-ion intermediate **99** (Scheme 58).

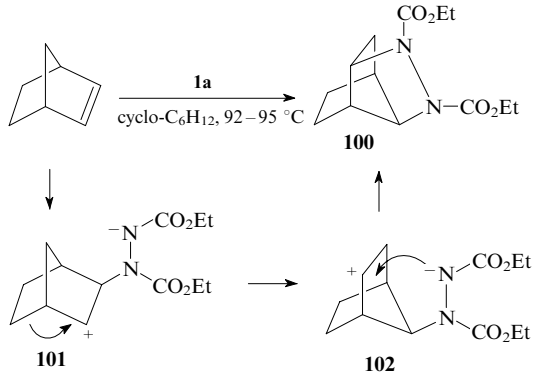
Scheme 58



R^1 = H, Me; R^2 = H, Me, Et

Norbornylene, which cannot form normal ene products of addition with reagent **1a**, gives polycyclic product **100** (Scheme 59). Presumably, in this case, the reaction also proceeds through the formation of zwitter-ion intermediates **101** and **102**. On the other hand, a free-radical mechanism is also possible for cyclic alkenes.

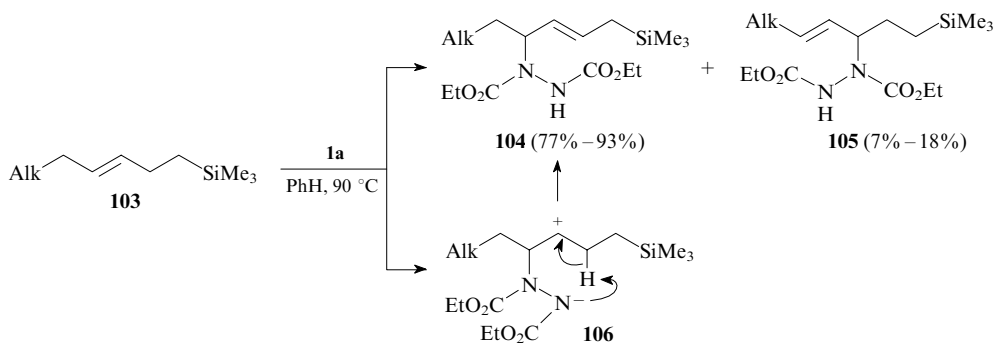
Scheme 59



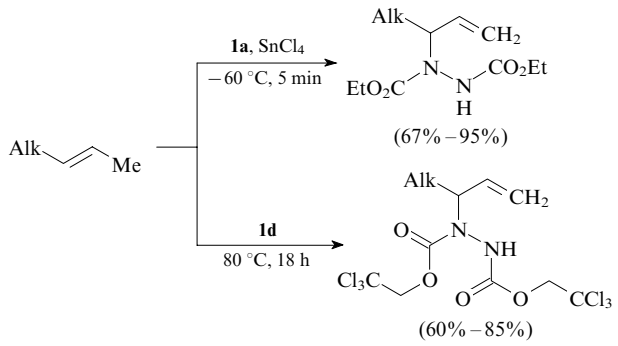
The reaction of DEAD with homoallylsilanes **103** leads to two products of addition **104** and **105**, the former clearly predominating (Scheme 60).[171] This fact can be explained by the stabilization of intermediate **106** by hyperconjugation with trimethylsilyl groups (γ-effect).[172]

The reaction of azodicarboxylate **1d** with alkenes carried out with thermal activation requires 18 h for process completion.[173] At the same time, upon application of tin tetrachloride as a Lewis acid, the time of reaction of alkenes with DEAD is 5 min (Scheme 61).[174]

Scheme 60

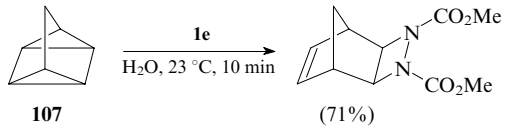


Scheme 61



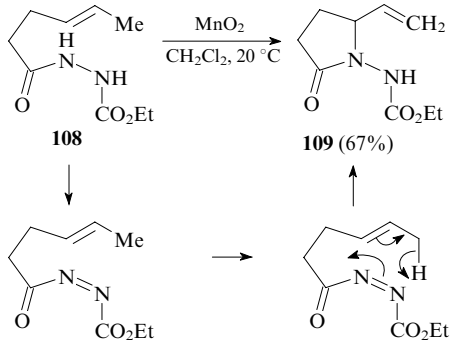
An important role in the ene reaction is played by the solvent nature.[175] Thus, if the solvent has the electrophilic nature, the process is accelerated. If the solvent is nucleophilic, then the reaction rate decreases. For example, the rate of reaction of compound **1a** with 2-methylbut-2-ene is 40 times higher in benzyl alcohol than in n-hexane. The process is accelerated even more appreciably if an organic solvent is replaced by water. Thus, the addition of azodicarboxylate **1d** to cyclohexene in an aqueous emulsion proceeds for 8 h, whereas the reaction in benzene completes only in 24 h.[176] Similar acceleration was also noted upon cycloaddition of reagent **1e** to quadricyclane (**107**) (Scheme 62).[176–179]

Scheme 62



An intramolecular modification of the ene reaction is observed upon oxidation of hydrazide **108** with activated manganese(IV) oxide, which results in pyrrolidone **109**.[180, 181] A tentative mechanism of this transformation is presented in Scheme 63.

Scheme 63

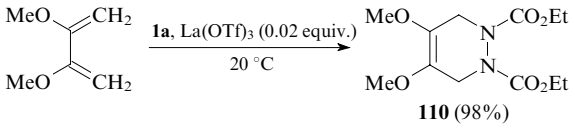


The ene reaction of DEAD with soybean oil proceeds at room temperature, resulting in a polymer product.[182] It was shown that the viscosity of a mixture of **1a** and soybean oil increases by a factor of 300 in 14 days, and the mixture can be used as an environmentally safe self-curing material.

The behaviour of azodicarboxylates in the Diels–Alder reaction has been studied in sufficient detail. These compounds are very active dienophiles.[183] Thus, even at room temperature, they form the products of [4 + 2]-cycloaddition with dienes bearing electron-donating substituents.[184] Inactive dienes add azo compounds under thermal or microwave initiation.[185–188]

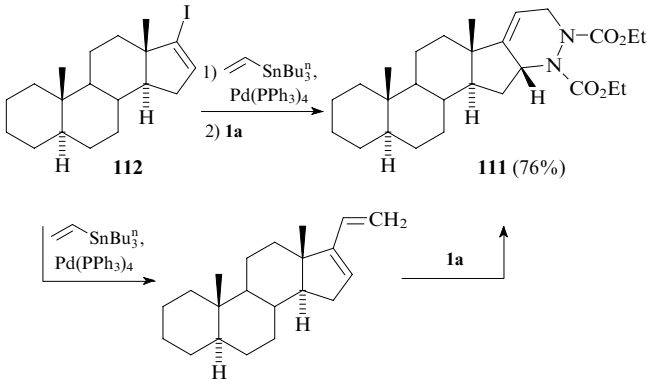
A promising catalyst for cycloaddition of dienes to azodicarboxylates is lanthanum triflate. In its presence, tetrahydropyridazine **110** was obtained in a high yield (Scheme 64).[189] This reaction is carried out without a solvent, so that the catalyst is recovered with an insignificant loss in the activity.

Scheme 64



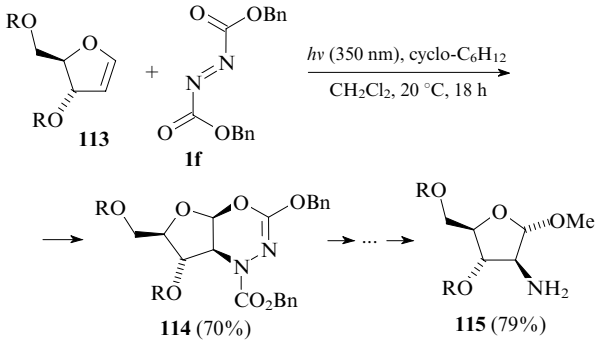
The Stille and Diels–Alder reactions were performed as a one-pot process to prepare tetrahydropyridazine **111** annulated with a five-membered steroid ring **112** (Scheme 65).[190]

Scheme 65



Leblanc and co-workers[191–195] showed that azodicarboxylates can participate in the Diels–Alder reaction as heterodienes. Thus, the reaction of dihydrofuran **113** with compound **1f** yielded [4 + 2]-cycloaddition products **114**, which were further converted to 2-aminofuranozide **115** (Scheme 66).

Scheme 66

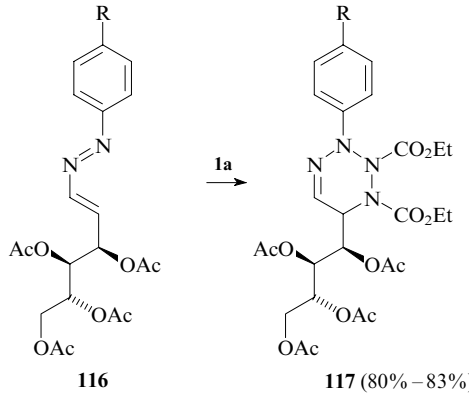


R = $SiBu^tPh_2$

Reagent **1a** reacts with heterodiene **116** under conditions of microwave activation, giving tetrahydrotetrazine derivatives **117** in high yields (Scheme 67).[196]

An example of 1,3-dipolar cycloaddtion to azodicarboxylates is ring transformation of thiadiazole **118** spiro-fused to the adamantane cage induced by compound **1e** (Scheme 68).[197] Obviously, in the beginning, the corre-

Scheme 67

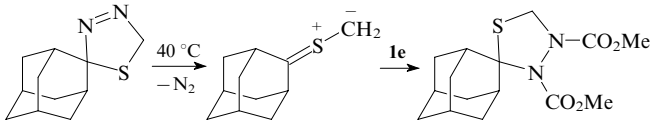


116 **117** (80%–83%)

R = H, Cl, Me, OMe

sponding sulfur ylide is formed from the spiro ring, and then it reacts with dimethyl azodicarboxylate.

Scheme 68



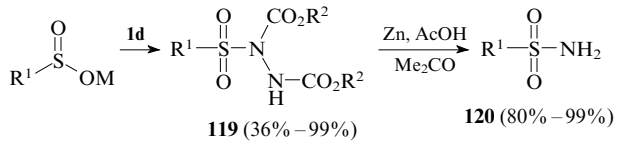
118 (57%)

IV. Azodicarboxylates as oxidants

Alcohols are oxidized with azodicarboxylates to the corresponding aldehydes or ketones in the presence of various catalysts such as CuCl,[198,199] $ZnBr_2$ [200] or aminoxyl radicals.[201] Under action of DEAD, thiols and thiophenols are converted to symmetrical [202] or unsymmetrical disulfides.[203,204] Disubstituted sulfides form sulfoxides with this reagent.[205]

The salts of alkyl- and arylsulfinic acids are oxidized with compound **1d** to sulfonylhydrazines **119**, which can be subsequently reduced to sulfonamides **120** (Scheme 69).[206]

Scheme 69



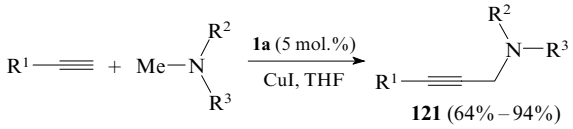
119 (36%–99%) **120** (80%–99%)

R^1 = Ar, Het, Bu^n; R^2 = CH_2CCl_3; M = Na, Li

On treatment with azodicarboxylates, alkylamines are oxidized to imines which then can be transformed into amines and the corresponding carbonyl compounds.[207–209] Moreover, imines generated *in situ* can react with various nucleophiles. Thus, under the action of the CuI–DEAD system, the regioselective alkynylation of tertiary methylamines with termianl alkynes was accomplished.[210] The active species of this transformation is iminium salt that results from the reaction of amine with compound **1a**. Alkynylamines **121** are formed in high yields under mild conditions, and there is no need to protect the reaction mixture from air and moisture (Scheme 70).

The fluoromethylation of tertiary amines with fluorine-containing sulfones in the presence of reagent **1b** giving amines **122** was described [211] (Scheme 71). First, the amine

Scheme 70

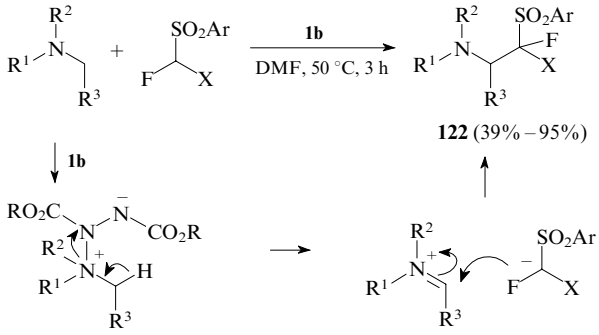


121 (64%–94%)

R^1 = Ar, Het, $SiMe_3$, Bn; R^2, R^3 = Me, Pr^i, Bu^t, cyclo-C_5H_9, cyclo-C_6H_{11}, Bn

is likely to add to azodicarboxylate to form a zwitterion intermediate in which a 1,4-shift of the proton takes place to give imine that is attacked by the anion.

Scheme 71

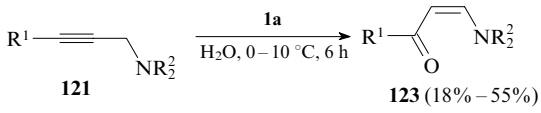


122 (39%–95%)

R^1, R^2, R^3 = Alk; X = SO_2Ph, CO_2Et; Ar = Ph, 2-Py; Py is pyridyl

Note that compounds **121** are oxidized by DEAD in the presence of water exclusively into *cis*-enamines **123** (Scheme 72).[212]

Scheme 72

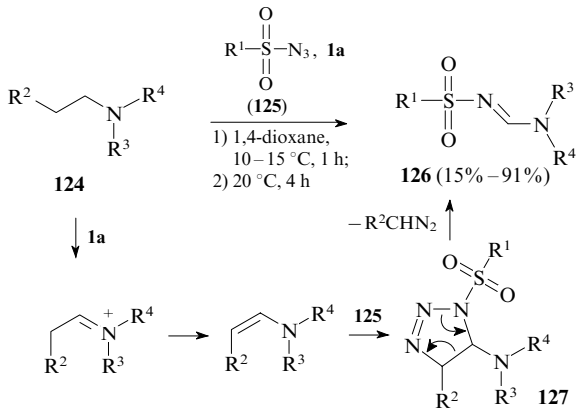


121 **123** (18%–55%)

R^1 = Alk; R^2 = Alk, Ar, Het

However, the dehydrogenation of amines **124** with diethyl azodicarboxylate in the presence of sulfonyl azide **125** leads to sulfonylamidine **126** (Scheme 73).[213] The authors assume that the reaction proceeds through the cycloaddition of sulfonyl azide to the *in situ* generated enamine followed by elimination of the diazolalkane molecule from triazole **127**.

Scheme 73

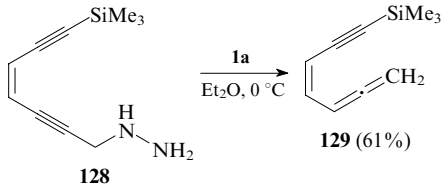


124 **126** (15%–91%) **127**

R^1 = Alk, Ar, Het; R^2, R^3, R^4 = H, Me, Et, Ph, Bn

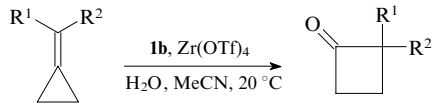
On treatment with reagent **1a**, polyunsaturated hydrazine **128** is transformed into allene **129** (Scheme 74).[214]

Scheme 74



In the presence of zirconium triflate, methylenecyclopropanes **130** react with diisopropyl azodicarboxylate (**1b**), resulting in cyclobutanones **131** (Scheme 75).[215]

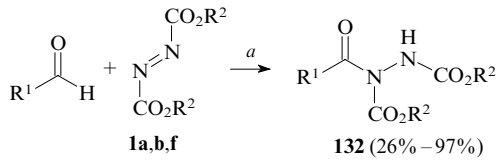
Scheme 75



R^1, R^2 = Me, Ph, 4-$MeOC_6H_4$, 4-MeC_6H_4, 4-FC_6H_4, 4-ClC_6H_4, 4-BrC_6H_4

The reaction of aldehydes with azodicarboxylates leads to acid hydrazides **132** (Scheme 76). The addition occurs at room temperature both in the presence of a catalyst[216] and without a catalyst.[217,218]

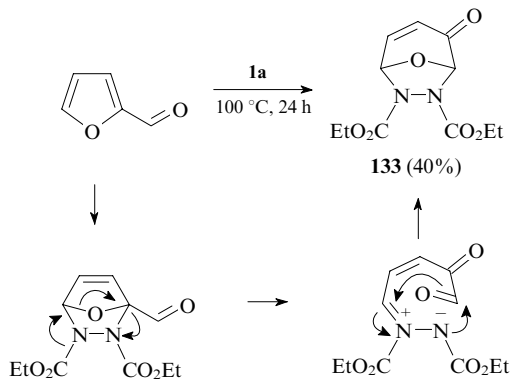
Scheme 76



(*a*) $[Rh(OAc)_2]_2$, EtOAc, 25 °C, 12–120 h;
R^1 = Alk, Ar; R^2 = Et, Pr^i, Bn

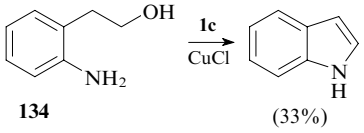
The [3.2.1]bicyclic compound **133** is the major product formed in the reaction of furfural with diethyl azodicarboxylate (**1a**).[219] A tentative mechanism of its formation is presented in Scheme 77.

Scheme 77



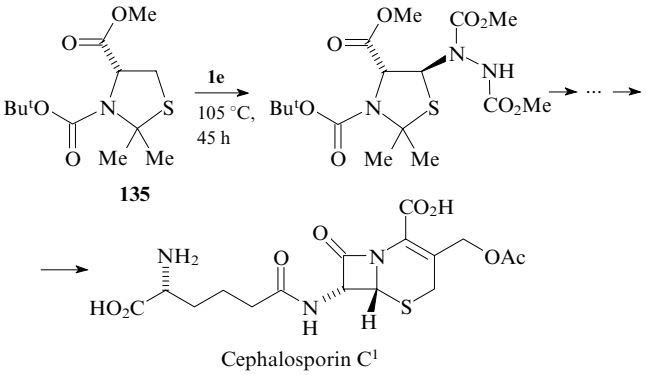
Azodicarboxylates can be used for dehydrogenation of dihydroquinolines and tetrahydrodiazepinoquinoxalines.[220–222] On treatment with di-*tert*-butyl azodicarboxylate (**1c**) in the presence of copper(I) chloride, alcohol **134** is oxidized with cyclization to indole (Scheme 78).[223]

Scheme 78



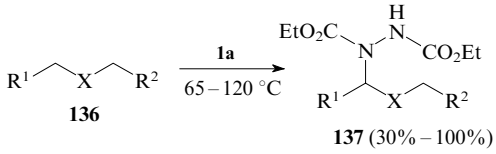
For the first time, functionalization of the activated C(sp^3)–H bond in organic compounds with participation of azodicarboxylates was used by Woodward *et al.*[224] in the total synthesis of cephalosporin C[1] (Scheme 79). The starting compound was chiral thiazolidine **135** to which reagent **1e** was added.

Scheme 79



Subsequently, the scope of application of this reaction was extended to ethers and dialkyl sulfides. Thus, the reaction of azodicarboxylate **1a** with compound **136** afforded hydrazines **137** in moderate to high yields (Scheme 80).[225] This process is most likely to occur by a radical mechanism.

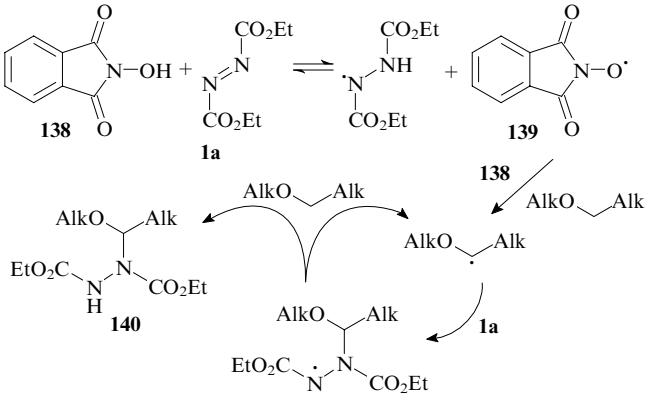
Scheme 80



R^1, R^2 = Alk, Bn, Ph; X = O, S

The use of *N*-hydroxyphthalimide (**138**) as a precursor of phthalimide-*N*-oxyl radical facilitates the addition of azo derivative **1a** to the C–H bond of ethers, thus enabling the process to be performed under mild conditions. This is

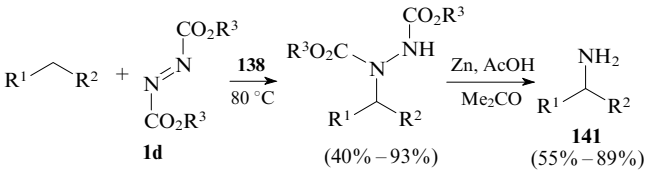
Scheme 81



apparently due to oxidation of *N*-hydroxyphthalimide with azodicarboxylate into *N*-oxyl radical **139**, which triggers the chain reaction leading to products **140** (Scheme 81).[226]

Further invetsigations showed that this oxidizing system is efficient not only for the transformation of ethers but can also be used for the functionalization of alkylarenes and cycloalkanes (Scheme 82).

Scheme 82

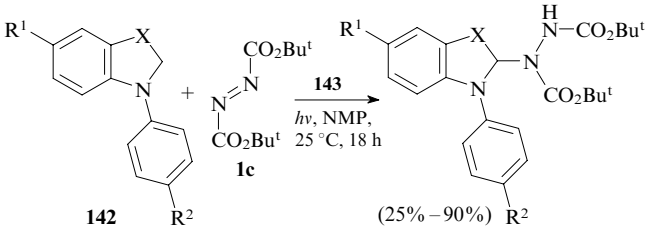


R^1, R^2 = Alk, Ar, Het; R^3 = CH_2CCl_3

For example, this method was used to obtain amines **141** in good yields.[227]

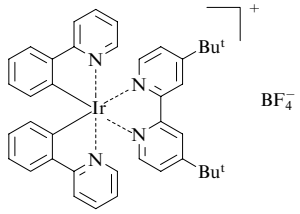
A photochemical modification of this transformation was suggested by Nishibayashi's research group.[228] The reaction of benzannulated heterocycles of common formula **142** with azodicarboxylate **1c** requires the presence of iridium complex **143** and allows for the introduction of a hydrazine moiety into the heterocyclic molecule at room temperature (Scheme 83).

Scheme 83



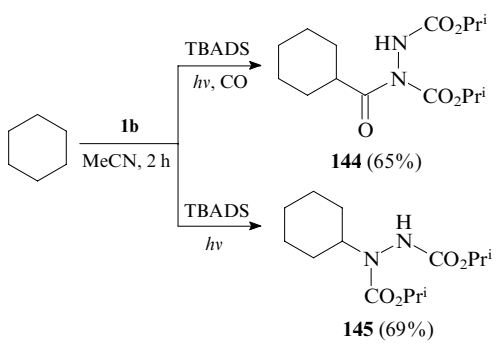
R^1 = H, Me; R^2 = H, Me, OMe, Cl, Bu^t, CO_2Bu^t;
X = CH_2, $(CH_2)_2$, $(CH_2)_3$, SCH_2, OCH_2, N(Ac)CH_2;
NMP is *N*-methylpyrrolidone;

143 =



The application of tetra-n-butylammonium decatungstate $[(Bu^n_4N)_4[W_{10}O_{32}]$, TBADT) as a photocatalyst facilitates the insertion of reagent **1b** at the C–H bond of ethers, cycloalkanes, and aldehydes, resulting in the corresponding hydrazides and hydrazines in good yields (*e.g.*, compounds **144** and **145** in Scheme 84).[229] Moreover, under these conditions, the C–H carbonylation of cycloalkanes and addition of azodicarboxylates to the resulting aldehydes can be carried out in a one-pot procedure.

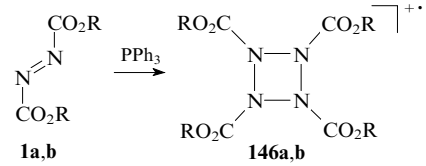
Scheme 84



V. Transformations occurring under the Mitsunobu reacion conditions

As it was mentioned in the Introduction, the **1**–PPh_3 reagent system is the key system for the Mitsunobu reaction.[14–19] The present Section covers transformations that occur under similar conditions but do not relate to the Mitsunobu reaction. Thus, Australian researchers[230] used EPR spectroscopy to demonstrate that cyclic radical cations **146a**,**b** are formed in solutions of triphenylphosphine and azodicarboxylates **1a**,**b** (Scheme 85).

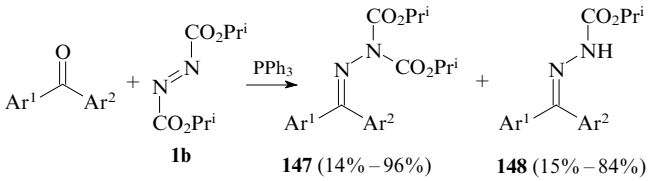
Scheme 85



R = Et (**a**), Pr^i (**b**)

Of particular interest is the behaviour of carbonyl compounds under the Mitsunobu reacion conditions. Thus, diaryl ketones are converted to hydrazones **147** and **148** (Scheme 86).[231] It was shown that the product ratio depends on the ratio of diaryl ketone and the Huisgen zwitter-ion. Thus, as the amounts of PPh_3 and azodicarboxylate **1b** increase, the yield of compound **148** increases and reaches 84% at the aldehyde : compound **1b** : PPh_3 ratio of 1 : 3 : 3.

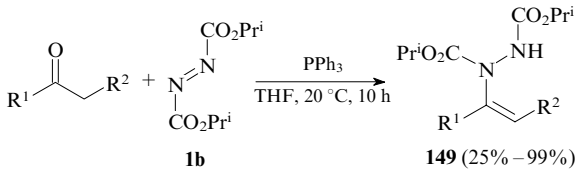
Scheme 86



Ar^1, Ar^2 = Ph, 4-ClC_6H_4, 3-MeC_6H_4, 4-MeC_6H_4, 4-$Bu^tC_6H_4$

However, if an alkyl is present instead of one of the aryl substituents, enehydrazine **149** is formed as the only reaction product (Scheme 87).[232, 233]

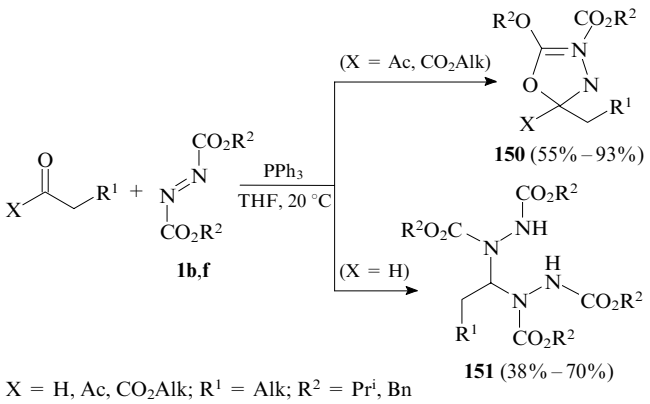
Scheme 87



R^1 = Alk, Ar; R^2 = Alk

It was also reported that under these conditions, 1,2-dicarbonyl compounds form cyclic products **150**, whereas aliphatic aldehydes afford bis(hydrazines) **151** (Scheme 88).[233]

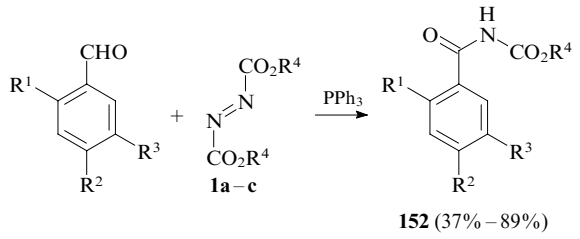
Scheme 88



X = H, Ac, CO_2Alk; R^1 = Alk; R^2 = Pr^i, Bn

The reaction of aromatic aldehydes with dialkyl azodicarboxylates **1a–c** in the presence of triphenylphosphine yields acylcarbamates **152** (Scheme 89).[234]

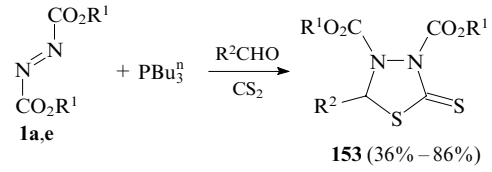
Scheme 89



R^1 = H, F; R^2 = H, F, Cl, Br, CF_3, NO_2; R^3 = H, F, Cl, NO_2; R^4 = Et, Pr^i, Bu^t

However, a similar reaction carried out in carbon disulfide and in the presence of tri-n-butylphosphine gives 1,3,4-thiadiazolidine-2-thione **153** as the major product (Scheme 90).[235]

Scheme 90

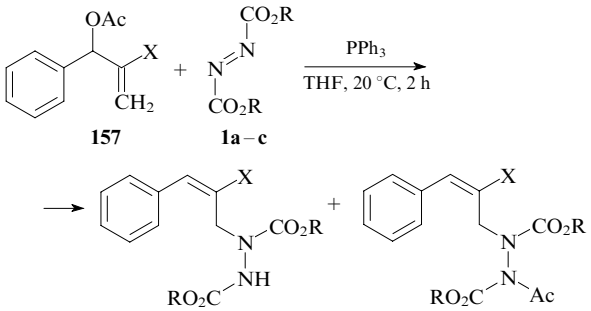


R^1 = Me, Et; R^2 = Ph, 4-$O_2NC_6H_4$, 4-ClC_6H_4, 2-furyl

Under the Mitsunobu reaction conditions, 3-formylchromones **154** form tricyclic products **155** and **156** (Scheme 91).[236] It was found that the ratio of these products remains unchanged even upon application of three-fold excess of the azo compound.

Under the Mitsunobu reacion conditions, terminal alkenes **157** are converted to compounds **158** and **159** (Scheme 92).[237]

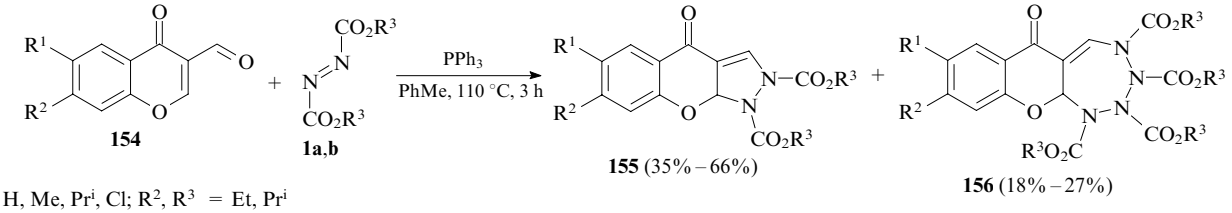
Scheme 92



R = Et, Pr^i, Bu^t; X = CO_2Me, CN

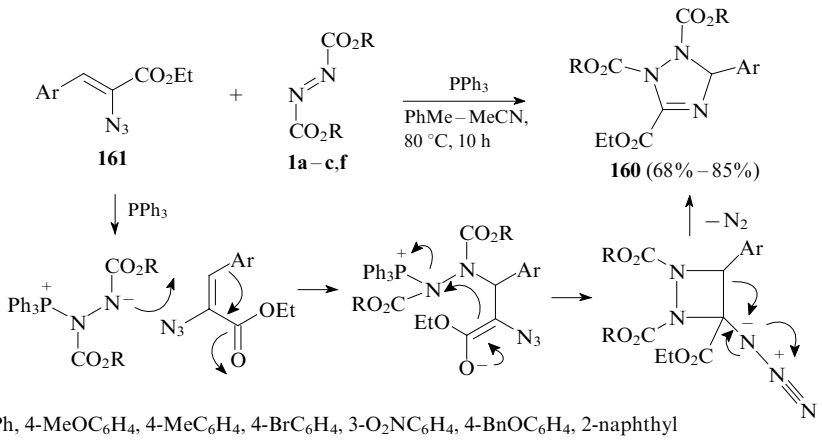
A large series of 1,2,4-triazolines **160** were synthesized from 2-azidoacrylates **161** and dialkyl azodicarboxylates in the presence of a catalytic amount of triphenylphosphine.[238]

Scheme 91



R^1 = H, Me, Pr^i, Cl; R^2, R^3 = Et, Pr^i

Scheme 93



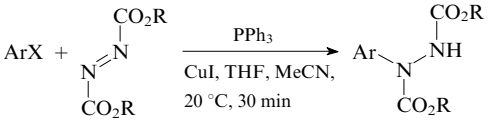
R = Et, Pr^i, Bu^t, Bn; Ar = Ph, 4-$MeOC_6H_4$, 4-MeC_6H_4, 4-BrC_6H_4, 3-$O_2NC_6H_4$, 4-$BnOC_6H_4$, 2-naphthyl

The sequence of transformations that demonstrates a proposed mechanism is depicted in Scheme 93.

Under the Mitsunobu reacion conditions, various arylamines can be converted to aryliminophosphoranes in high yields.[239]

Arylhydrazines **162** are formed from aryl halides and azodicarboxylates **1a**,**b** in the presence of triphenylphosphine and univalent copper iodide (Scheme 94).[240]

Scheme 94

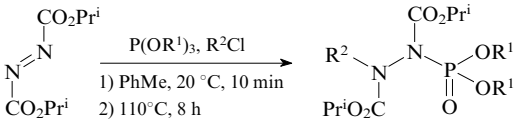


1a,**b** **162** (76%–91%)

R = Et, Pr^i; Ar = 3-MeC$_6$H$_4$, 4-NCC$_6$H$_4$, 2-O$_2$NC$_6$H$_4$, 3-F$_3$CC$_6$H$_4$, 1-naphthyl, 2-thienyl; X = Br, I

Hydrazinophosphonates **163** were obtained in high yields from diisopropyl azodicarboxylate (**1b**) under modified Morrison reaction conditions (Scheme 95).[241]

Scheme 95



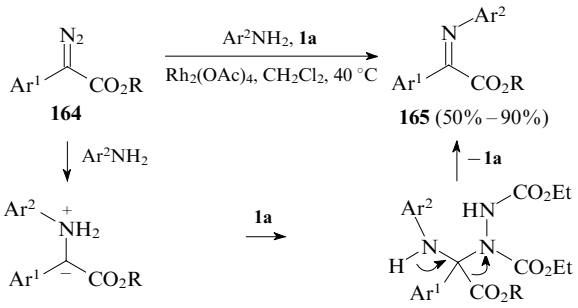
1b **163** (85%–95%)

R^1 = Me, Et; R^2 = ArC(O), ArSO$_2$, (PhO)$_2$P(O)

VI. Miscellanous reactions

Diazo compounds **164** react with arylamines in the presence of DEAD and rhodium acetate to furnish imines **165** (Scheme 96).[242] The authors assume that initially the corresponding zwitter-ion intermediate is generated from the diazo compound and amine. The intermediate adds to reagent **1a**. In this process, water can be used as a nucleophile instead of amine.[243]

Scheme 96

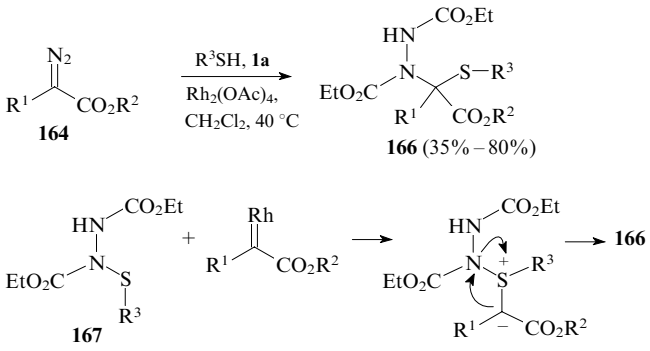


164 **165** (50%–90%)

Ar^1 = Ph, 4-MeOC$_6$H$_4$, 4-ClC$_6$H$_4$, 4-O$_2$NC$_6$H$_4$;
Ar^2 = Ph, 4-O$_2$NC$_6$H$_4$, 2-MeOC$_6$H$_4$; R = Me, Pr^i, Bu^t

If the thiol serves as the nucleophile, hydrazine **166** is the major reaction product (Scheme 97).[244] In this case, the key stage seems to be the reaction of adduct **167** with intermediate rhodium complex.

Scheme 97



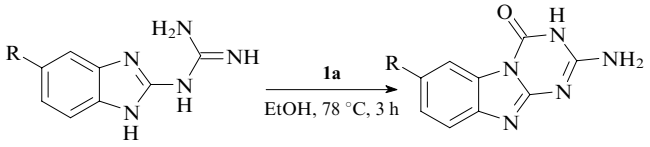
164 **166** (35%–80%)

167

R^1 = Ph, 4-O$_2$NC$_6$H$_4$, CO$_2$Me; R^2 = H, Me;
R^3 = Et, Pr^i, Bn, Ph, 4-O$_2$NC$_6$H$_4$, 4-MeOC$_6$H$_4$

Benzimidazoles **168** cyclize under the action of DEAD into heterocyclic systems **169** (Scheme 98).[245] This reaction is a rare example of C-electrophilic behaviour of azodicarboxylates.

Scheme 98



168 **169**

R = H (yield 76%), Me (57%)

* * *

In conclusion, note that dialkyl azodicarboxylates are interesting and promising reagents for fine organic synthesis. They are used, first of all, as N-electrophiles and powerful dienophiles in the Diels—Alder reaction. These derivatives showed their efficiency in the introduction of a hydrazine function into the aromatic core and in the formation of an asymmetric centre at the α-position of the carbonyl compounds. Nowadays, the field of C–H-functionalization of various substrates involving azodicarboxylates is rapidly developing. However, despite the fact that these methods have been extensively studied and are general, there is a plethora of examples when the reaction products differ from the products predicted theoretically. We hope that the chemistry of azodicarboxylates will further develop, thus extending the scope of their application in fine organic synthesis.

References

1. J M Harris, E A Bolessa, A J Mendonca, S-C Feng, J C Vederas *J. Chem. Soc., Perkin Trans. 1* 1945 (1995)
2. B H Lipshutz, D W Chung, B Rich, R Corral *Org. Lett.* **8** 5069 (2006)
3. R C Cookson, S S H Gilani, I D R Stevens *Tetrahedron Lett.* **3** 615 (1962)
4. M A Brimble, C H Heathcock, G N Nobin *Tetrahedron: Asymmetry* **7** 2007 (1996)
5. R M Moriarty, I Prakash, R Penrnasta *Synth. Commun.* **17** 409 (1987)
6. P Loew, C D Weis *J. Heterocycl. Chem.* **13** 829 (1976)

7. J T Starr, G S Rai, H Dang, B J McNelis *Synth. Commun.* **27** 3197 (1997)
8. D Mackay, D D McIntyre *Can. J. Chem.* **62** 355 (1984)
9. D A Holden *Can. J. Chem.* **62** 574 (1984)
10. H Konishi, T Y Lam, J P Malerich, V H Rawal *Org. Lett.* **12** 2028 (2010)
11. H Mitchell, Y Leblanc *J. Org. Chem.* **59** 682 (1994)
12. O Diels, P Fritzsche *Ber. Dtsch. Chem. Ges.* **44** 3026 (1911)
13. D Morrison *J. Org. Chem.* **23** 1072 (1958)
14. O Mitsunobu, M Yamada *Bull. Chem. Soc. Jpn.* **40** 2380 (1967)
15. O Mitsunobu *Synthesis* 1 (1981)
16. D L Hughes *Org. Prep. Proced. Int.* **28** 127 (1996)
17. K C Kumara Swamy, N N Bhuvan Kumar, E Balaraman, K V P Pavan Kumar *Chem. Rev.* **109** 2551 (2009)
18. A J Reynolds, M Kassiou *Curr. Org. Chem.* **13** 1610 (2009)
19. N E Golantsov, A V Karchava, M A Yurovskaya *Chem. Heterocycl. Compd. (Engl. Transl.)* **44** 263 (2008) [*Khim. Geterotsikl. Soedin.* 347 (2008)]
20. E Fahr, H Lind *Angew. Chem., Int. Ed. Engl.* **5** 372 (1966)
21. K Mackenzie, in *Chemistry of the Hydrazo, Azo and Azoxy Groups* (Ed. S Patai) (New York: Wiley, 1975) Ch. 11
22. G Bianchi, C de Micheli, R Gandolfy, in *The Chemistry of the Double Bonded Functional Groups* (Ed. S Patai) (New York: Wiley, 1977) Ch. 6
23. A.P.Marchand, in *The Chemistry of the Double Bonded Functional Groups* (Ed. S Patai) (New York: Wiley, 1977) Ch. 7
24. C J Moody *Adv. Heterocycl. Chem.* **30** 1 (1980)
25. X Xu, G Cheng, X Li *Chin. J. Org. Chem.* **32** 1024 (2012)
26. V Nair, A T Biju, C M Smitha, P B Beneesh *Chem. – Asian J.* **3** 810 (2008)
27. A M R Smith, K K (Mimi) Hii *Chem. Rev.* **111** 1637 (2011)
28. A Russo, C De Fusco, A Lattanzi *RSC Adv.* **2** 385 (2012)
29. E Erdik, M Ay *Chem. Rev.* **89** 1947 (1989)
30. S H Schroeter *J. Org. Chem.* **34** 4012 (1969)
31. I Zaltsgendler, Y Leblanc, M A Bernstein *Tetrahedron Lett.* **34** 2441 (1993)
32. Y Leblanc, N Boudreault *J. Org. Chem.* **60** 4268 (1995)
33. J S Yadav, B V S Reddy, G M Kumar, C Madan *Synlett* 1781 (2001)
34. J S Yadav, B V S Reddy, G Veerendhar, R Srinivasa Rao, K Nagaiah *Chem. Lett.* **31** 318 (2002)
35. S M Inamdar, V K More, S K Mandal *Tetrahedron Lett.* **54** 530 (2013)
36. K Y Lee, Y J Im, T H Kim, J N Kim *Bull. Korean Chem. Soc.* **22** 131 (2001)
37. C Li, C Chan, A C Heimann, S J Danishefsky *Angew. Chem., Int. Ed.* **46** 1448 (2007)
38. A S Kolesnikova, A M Zhirov, I V Aksenova, A V Aksenov *Chem. Heterocycl. Compd. (Engl. Transl.)* **48** 1410 (2012) [*Khim. Geterotsikl. Soedin.* 1513 (2012)]
39. A M Zhirov, A S Kolesnikova, I V Aksenova, A S Lyakhovnenko, A V Aksenov *Russ. Chem. Bull., Int. Ed.* **62** 1125 (2013) [*Izv. Akad. Nauk, Ser. Khim.* 1125 (2013)]
40. L Gu, B S Neo, Y Zhang *Org. Lett.* **13** 1872 (2011)
41. R Lenaršič, M Kočevar, S Polanc *J. Org. Chem.* **64** 2558 (1999)
42. S Bombek, R Lenaršič, M Kočevar, L Saint-Jalmes, J-R Desmurs, S Polanc *Chem. Commun.* 1494 (2002)
43. S Bombek, F Požgan, M Kočevar, S Polanc *J. Org. Chem.* **99** 2224 (2004)
44. T Stropnik, S Bombek, M Kočevar, S Polanc *Tetrahedron Lett.* **49** 1729 (2008)
45. G W Breton *Tetrahedron Lett.* **52** 733 (2011)
46. G W Breton, K R Hoke *J. Org. Chem.* **78** 4697 (2013)
47. H Ban, J Gavrilyuk, C F Barbas III *J. Am. Chem. Soc.* **132** 1523 (2010)
48. H Ban, M Nagano, J Gavrilyuk, W Hakamata, T Inokuma, C F Barbas III *Bioconjug. Chem.* **24** 520 (2013)
49. M W Rommi *Cell. Mol. Life Sci.* **28** 882 (1972)
50. C K Lee, S J Kim, C S Hahn *J. Org. Chem.* **45** 1692 (1980)
51. C K Lee, Y M Ahn *J. Org. Chem.* **55** 3957 (1990)
52. E C Taylor, F Sowinski *J. Am. Chem. Soc.* **90** 1374 (1968)
53. A D Allen, W Huang, P A Moore, A R Far, T T Tidwell *J. Org. Chem.* **65** 5676 (2000)
54. S Brandes, M Bella, A Kjærsgaard, K A Jørgensen *Angew. Chem., Int. Ed.* **45** 1147 (2006)
55. J T Kuethe, I W Davies *Tetrahedron Lett.* **45** 4009 (2004)
56. L Cheng, L Li, D Wang, Y-J Chen *Org. Lett.* **11** 3874 (2009)
57. T Bui, M Borregan, C F Barbas III *J. Org. Chem.* **74** 8935 (2009)
58. S Mouri, Z Chen, H Mitsunuma, M Furutachi, S Matsunaga, M Shibasaki *J. Am. Chem. Soc.* **132** 1255 (2010)
59. Z Yang, Z Wang, S Bai, X Liu, L Lin, X Feng *Org. Lett.* **13** 596 (2011)
60. M Šimek, M Remeš, J Veselý, R Rios *Asian J. Org. Chem.* **2** 64 (2013)
61. T Mashiko, K Hara, D Tanaka, Y Fujiwara, N Kumagai, M Shibasaki *J. Am. Chem. Soc.* **129** 11342 (2007)
62. T Mashiko, N Kumagai, M Shibasaki *Org. Lett.* **10** 2725 (2008)
63. F Palacios, C Alonso, G Rubiales, M Villegas *Tetrahedron* **65** 1119 (2009)
64. C Yamazaki, H Arima, S Udagawa *J. Heterocycl. Chem.* **33** 41 (1996)
65. J P Demers, D H Klaubert *Tetrahedron Lett.* **28** 4933 (1987)
66. R Velarde-Ortiz, A Guijarro, R D Rieke *Tetrahedron Lett.* **39** 9157 (1998)
67. J-C Blazejewski, P Diter, T Warchol, C Wakselman *Tetrahedron Lett.* **42** 859 (2001)
68. O Tšubrik, R Sillard, U Mäeorg *Synthesis* 843 (2006)
69. R E Beveridge, R A Batey *Org. Lett.* **14** 540 (2012)
70. W J Kinart, C M Kinart *J. Organomet. Chem.* **665** 233 (2003)
71. W J Kinart, C M Kinart *J. Organomet. Chem.* **691** 1441 (2006)
72. W J Kinart, C M Kinart, R Oszczeda, Q T Trana *Catal. Lett.* **103** 3 (2005)
73. W J Kinart, C M Kinart, Q T Tran, R Oszczeda, R B Nazarski *Appl. Organomet. Chem.* **18** 398 (2004)
74. M Inman, C J Moody *Chem. Commun.* **47** 788 (2011)
75. M Inman, A Carbone, C J Moody *J. Org. Chem.* **77** 1217 (2012)
76. K Kisseljova, O Tšubrik, R Sillard, S Mäeorg, U Mäeorg *Org. Lett.* **8** 43 (2006)
77. T Uemura, N Chatani *J. Org. Chem.* **70** 8631 (2005)
78. K Muñiz, A Iglesias *Angew. Chem., Int. Ed.* **46** 6350 (2007)
79. O Tšubrik, K Kisseljova, U Mäeorg *Synlett* 2391 (2006)
80. L Zhang, Z Tan *Tetrahedron Lett.* **41** 3025 (2000)
81. A Yanagisawa, T Koide, K Yoshida *Synlett* 1515 (2010)
82. D K An, K Hirakawa, S Okamoto, F Sato *Tetrahedron Lett.* **40** 3737 (1999)
83. B S Gerstenberger, M R Rauckhorst, J T Starr *Org. Lett.* **11** 2097 (2009)
84. W-Y Yu, W N Sit, K-M Lai, Z Zhou, A S C Chan *J. Am. Chem. Soc.* **130** 3304 (2008)
85. J Waser, E M Carreira *Angew. Chem., Int. Ed.* **43** 4099 (2004)
86. J Waser, E M Carreira *J. Am. Chem. Soc.* **126** 5676 (2004)
87. J Waser, B Gaspar, H Nambu, E M Carreira *J. Am. Chem. Soc.* **128** 11693 (2006)
88. K D Bunker, N W Sach, Q Huang, P F Richardson *Org. Lett.* **13** 4746 (2011)
89. V A Schmidt, E J Alexanian *J. Am. Chem. Soc.* **133** 11402 (2011)
90. B Han, X-L Yang, R Fang, W Yu, C Wang, X-Y Duan, S Liu *Angew. Chem., Int. Ed.* **51** 8816 (2012)
91. Yu V Zeifman *Russ. Chem. Bull. Engl. Transl.* **47** 2479 (1998) [*Izv. Akad. Nauk, Ser. Khim.* 2562 (1998)]
92. A J Oelke, D J France, T Hofmann, G Wuitschike, S V Ley *Nat. Prod. Rep.* **28** 1445 (2011)

93. Y Zhao, Y Pan, S-B D Sima, C-H Tan *Org. Biomol. Chem.* **10** 479 (2012)
94. F Palacios, C Alonso, G Rubialesa, J M Ezpeleta *Tetrahedron* **60** 2469 (2004)
95. F Palacios, A M O de Retana, J Oyarzabal, J M Ezpeleta *Tetrahedron* **54** 2281 (1998)
96. Z-T Huang, Z-R Liu *Synthesis* 357 (1987)
97. J S Yadav, B V Subba Reddy, C Venugopal, B Padmavani *Tetrahedron Lett.* **45** 7507 (2004)
98. R Matsubara, F Berthiol, S Kobayashi *J. Am. Chem. Soc.* **130** 1804 (2008)
99. G Dessole, L Bernardi, B F Bonini, E Capitò, M Fochi, R P Herrera, A Ricci, G Cahiez *J. Org. Chem.* **69** 8525 (2004)
100. P Gmeiner, E Hummel *Synthesis* 1026 (1994)
101. P C B Page, M J McKenzie, S M Allina, D R Buckle *Tetrahedron* **56** 9 (2000)
102. C-S Chao, C-K Cheng, S-H Li, K Chen *Tetrahedron Lett.* **50** 333 (2009)
103. D A Evans, T C Britton, R L Dorow, J F Dellaria Jr *Tetrahedron* **44** 5525 (1988)
104. M A Ciufolini, N Xi *J. Org. Chem.* **62** 2320 (1997)
105. S M Allin, J Towler, S N Gaskell, B Saha, W P Martin, P C B Page, M Edgar *Tetrahedron* **66** 9538 (2010)
106. A Bøgevig, K Juhl, N Kumaragurubaran, W Zhuang, K A Jøgensen *Angew. Chem., Int. Ed.* **41** 1790 (2002)
107. B List *J. Am. Chem. Soc.* **124** 5656 (2002)
108. J-Y Fu, Q-C Yang, Q-L Wang, J-N Ming, F-Y Wang, X-Y Xu, L-X Wang *J. Org. Chem.* **76** 4661 (2011)
109. D G Blackmond, A Moran, M Hughes, A Armstrong *J. Am. Chem. Soc.* **132** 7598 (2010)
110. N S Chowdari, C F Barbas III *Org. Lett.* **7** 867 (2005)
111. R Ait-Youcef, K Sbargoud, X Moreau, Ch Greack *Synlett* 3007 (2009)
112. J-Y Fu, X-Y Xu, Y-Ch Li, Q-Ch Huang, L-X Wang *Org. Biomol. Chem.* **8** 4524 (2010)
113. A Nuzzi, A Massi, A Dondoni *Org. Lett.* **10** 4485 (2008)
114. C E Hartmann, Th Baumann, M Bächle, S Bräse *Tetrahedron: Asymmetry* **21** 1341 (2010)
115. X Ding, H-L Jiang, C-J Zhu, Y-X Cheng *Tetrahedron Lett.* **51** 6105 (2010)
116. A V Kurkin, A A Utkina, M A Yurovskaya *Chem. Heterocycl. Compd. (Engl. Transl.)* **44** 106 (2008) [*Khim. Geterotsikl. Soedin.* 127 (2008)]
117. N Kumaragurubaran, K Juhl, W Zhuang, A Bøgevig, K A Jørgensen *J. Am. Chem. Soc.* **124** 6254 (2002)
118. T-Y Liu, H-L Cui, Y Zhang, K Jiang, W Du, Z-Q He, Y-C Chen *Org. Lett.* **9** 3671 (2007)
119. P Kotrusz, S Alemayehu, Š Toma, H-G Schmalz, A Adler *Eur. J. Org. Chem.* 4904 (2005)
120. O Bortolini, L Caciolli, A Cavazzini, V Costa, R Greco, A Massi, L Pasti *Green Chem.* **14** 992 (2012)
121. A A Utkina, A V Kurkin, M A Yurovskaya *Chem. Heterocycl. Compd. (Engl. Transl.)* **48** 892 (2012) [*Khim. Geterotsikl. Soedin.* 960 (2012)]
122. S Gosiewska, R Soni, G J Clarkson, M Wills *Tetrahedron Lett.* **51** 4214 (2010)
123. Y Zhao, Y Pan, H Liu, Y Yang, Z Jiang, C-H Tan *Chem. – Eur. J.* **17** 3571 (2011)
124. M Terada, M Nakano, H Ube *J. Am. Chem. Soc.* **128** 16044 (2006)
125. L Simón, J M Goodman *J. Am. Chem. Soc.* **134** 16899 (2012)
126. X Xu, T Yabuta, P Yuan, Y Takemoto *Synlett* 137 (2006)
127. S M Kim, J H Lee, D Y Kim *Synlett* 2659 (2008)
128. R Zhu, D Zhang, J Wu, Ch Liu *Tetrahedron: Asymmetry* **18** 1655 (2007)
129. S H Jung, D Y Kim *Tetrahedron Lett.* **49** 5527 (2008)
130. C Liu, Q Zhu, K-W Huang, Y Lu *Org. Lett.* **13** 2638 (2011)
131. A Desmarchelier, H Yalgin, V Coeffard, X Moreau, C Greck *Tetrahedron Lett.* **52** 4430 (2011)
132. Y-Ch Chen *Synlett* 1919 (2008)
133. X Liu, H Li, L Deng *Org. Lett.* **7** 167 (2005)
134. P Pihko, A Pohjakallio *Synlett* 2115 (2004)
135. C-B Ji, Y-L Liu, X-L Zhao, Y-L Guo, H-Y Wang, J Zhou *Org. Biomol. Chem.* **10** 1158 (2012)
136. X Han, F Zhong, Y Lua *Adv. Synth. Catal.* **352** 2778 (2010)
137. S Saaby, M Bella, K A Jørgensen *J. Am. Chem. Soc.* **126** 8120 (2004)
138. M Marigo, K Juhl, K A Jørgensen *Angew. Chem., Int. Ed.* **42** 1367 (2003)
139. K Juhl, K A Jørgensen *J. Am. Chem. Soc.* **124** 2420 (2002)
140. M Marego, N Kumaragurubaran, K A Jørgensen *Synthesis* 957 (2005)
141. D A Evans, D S Johnson *Org. Lett.* **1** 595 (1999)
142. L Chang, Y Kuang, B Qin, X Zhou, X Liu, L Lin, X Feng *Org. Lett.* **12** 2214 (2010)
143. S Ghosh, M V Nandakumar, H Krautscheid, C Schneider *Tetrahedron Lett.* **51** 1860 (2010)
144. S M Kim, H R Kim, D Y Kim *Org. Lett.* **7** 2309 (2005)
145. J H Lee, H T Bang, D Y Kim *Synlett* 1821 (2008)
146. Y K Kang, D Y Kim *Tetrahedron Lett.* **47** 4565 (2006)
147. D A Evans, S G Nelson *J. Am. Chem. Soc.* **119** 6452 (1997)
148. M Meseguer, M Moreno-Mañas, A Vallribera *Tetrahedron Lett.* **41** 4093 (2000)
149. Y Hasegawa, M Watanabe, I D Gridnev, T Ikariya *J. Am. Chem. Soc.* **130** 2158 (2008)
150. T Mashiko, N Kumagai, M Shibasaki *J. Am. Chem. Soc.* **131** 14990 (2009)
151. Q-A Chen, W Zenga, Y-G Zhou *Tetrahedron Lett.* **50** 6866 (2009)
152. R He, X Wang, T Hashimoto, K Maruoka *Angew. Chem., Int. Ed.* **47** 9466 (2008)
153. R He, K Maruoka *Synthesis* 2289 (2009)
154. Q Lan, X Wang, R He, C Ding, K Maruoka *Tetrahedron Lett.* **50** 3280 (2009)
155. V Coeffard, A Desmarchelier, B Morel, X Moreau, C Greck *Org. Lett.* **13** 5778 (2011)
156. D Monge, K L Jensen, I Marín, K A Jørgensen *Org. Lett.* **13** 328 (2011)
157. N S Chowdari, D B Ramachary, C F Barbas III *Org. Lett.* **5** 1685 (2003)
158. S Ma, N Jiao, Z Zheng, Z Ma, Z Lu, L Ye, Y Deng, G Chen *Org. Lett.* **6** 2193 (2004)
159. W Shu, Q Yang, G Jia, S Ma *Tetrahedron* **64** 11159 (2008)
160. E Kianmehr, A Bakhtiary, C Zhu *Monatsh. Chem.* **143** 255 (2012)
161. Y Wang, F Peng, H Zhang, Z Shao *Synlett* 3287 (2009)
162. A J Oelke, S Kumarn, D A Longbottom, S V Ley *Synlett* 2548 (2006)
163. J Bezenšek, U Grošelj, K Stare, J Svete, B Stanovnik *Tetrahedron* **68** 516 (2012)
164. C Appayee, A J Fraboni, S E Brenner-Moyer *J. Org. Chem.* **77** 8828 (2012)
165. P Galzerano, F Pesciaioli, A Mazzanti, G Bartoli, P Melchiorre *Angew. Chem., Int. Ed.* **48** 7892 (2009)
166. A Kamimura, Y Gunjigake, H Mitsudera, S Yokoyama *Tetrahedron Lett.* **39** 7323 (1998)
167. M Shi, G-L Zhao *Tetrahedron* **60** 2083 (2004)
168. A Desmarchelier, V Coeffard, X Moreau, C Greck *Chem. – Eur. J.* **18** 13222 (2012)
169. B Qian, L Yang, H Huang *Tetrahedron Lett.* **54** 711 (2013)
170. W A Thaler, B Frazus *J. Org. Chem.* **29** 2226 (1964)
171. T K Sarkar, B K Ghorai, S K Das, P Gangopadhyay, P S V Subba Rao *Tetrahedron Lett.* **37** 6607 (1996)
172. J B Lamber *Tetrahedron* **46** 2677 (1990)
173. Y Leblanc, R Zamboni, M A Bernstein *J. Org. Chem.* **36** 1971 (1991)
174. M A Brimblel, C H Heathcock *J. Org. Chem.* **58** 5261 (1993)

175. G Desimoni, G Faita, P P Righetti, A Sfulcini, D Tsyganov *Tetrahedron* **50** 1821 (1994)
176. S Narayan, J Muldoon, M G Finn, V V Fokin, H C Kolb, K B Sharpless *Angew. Chem., Int. Ed.* **44** 3275 (2005)
177. A Chanda, V V Fokin *Chem. Rev.* **109** 725 (2009)
178. M-O Simon, C-J Li *Chem. Soc. Rev.* **41** 1415 (2012)
179. U M Lindstrom, in *Organic Reactions in Water: Principles, Strategies and Applications* (Oxford: Blackwell, 2007) p. 350
180. E Vedejs, G P Meier *Tetrahedron Lett.* **20** 4185 (1979)
181. M Scartozzi, R Grondin, Y Leblanc *Tetrahedron Lett.* **33** 5717 (1992)
182. A Biswas, B K Sharma, J L Willett, S Z Erhan, H N Cheng *Green Chem.* **10** 290 (2008)
183. D L Boger, S M Weinreb, in *Hetero Diels – Alder Methodology in Organic Synthesis* (San Diego, CA: Academic Press, 1987) p. 154
184. D Castagnolo, G Giorgi, R Spinosa, F Corelli, M Botta *Eur. J. Org. Chem.* 3676 (2007)
185. J-C Monbaliu, J Marchand-Brynaert *Tetrahedron Lett.* **49** 1839 (2008)
186. J-C Monbaliu, J Marchand-Brynaert *Synthesis* 1876 (2009)
187. J-C Monbaliu, B Tinant, D Peeters, J Marchand-Brynaert *Tetrahedron Lett.* **51** 1052 (2010)
188. G Jenner, R B Salem *J. Chem. Soc., Perkin Trans. 2* 1961 (1990)
189. M Curini, F Epifano, M C Marcotullio, O Rosati *Heterocycles* **55** 1599 (2001)
190. R Skoda-Foldös, L Kollár *Synthesis* 2939 (2006)
191. B J Fitzsimmons, Y Leblanc, J Rokach *J. Am. Chem. Soc.* **109** 285 (1987)
192. B J Fitzsimmons, Y Leblanc, N Chan, J Rokach *J. Am. Chem. Soc.* **110** 5229 (1988)
193. Y Leblanc, B J Fitzsimmons *Tetrahedron Lett.* **30** 2889 (1989)
194. Y Leblanc, B J Fitzsimmons, J P Springer, J Rokach *J. Am. Chem. Soc.* **111** 2995 (1989)
195. R Grondin, Y Leblanc, K Hoogsteenl *Tetrahedron Lett.* **32** 5021 (1991)
196. M Avalos, R Babiano, P Cintas, F R Clemente, J L Jiménez, J C Palacios, J B Sánchez *J. Org. Chem.* **64** 6297 (1999)
197. R Huisgen, X Li, G Mloston, R Knorr, H Huber, D S Stephenson *Tetrahedron* **55** 12783 (1999)
198. I E Markó, A Gautier, J-L Mutonkole, R Dumeunier, A Ates, C J Urch, S M Brown *J. Organomet. Chem.* **624** 344 (2001)
199. T Nishii, T Ouchi, A Matsuda, Y Matsubara, Y Haraguchi, T Kawano, H Kaku, M Horikawa, T Tsunoda *Tetrahedron Lett.* **53** 5880 (2012)
200. H T Cao, R Grée *Tetrahedron Lett.* **50** 1493 (2009)
201. M Hayashi, M Shibuya, Y Iwabuchi *J. Org. Chem.* **77** 3005 (2012)
202. K Kato, O Mitsunobu *J. Org. Chem.* **35** 4227 (1970)
203. T Mukaiyama, K Takahashi *Tetrahedron Lett.* **9** 5907 (1968)
204. G R Morais, R A Falconer *Tetrahedron Lett.* **48** 7637 (2007)
205. R Axen, M Chaykovsky, B Witkop *J. Org. Chem.* **32** 4117 (1967)
206. W Y Chan, C Berthelette *Tetrahedron Lett.* **43** 4537 (2002)
207. J Kroutil, T Trnka, M Černý *Synthesis* 446 (2004)
208. P W Jeffs, H F Campbell, L Hawks *J. Chem. Soc. D* 1338 (1971)
209. J Kroutil, T Trnka, M Černý *Org. Lett.* **2** 1681 (2000)
210. X Xu, X Li *Org. Lett.* **11** 1027 (2009)
211. W Huang, C Ni, J Hu *New J. Chem.* **37** 1684 (2013)
212. X Xu, P Du, D Cheng, H Wang, X Li *Chem. Commun.* **48** 1811 (2012)
213. X Xu, X Li, L Ma, N Ye, B Weng *J. Am. Chem. Soc.* **130** 14048 (2008)
214. A G Myers, N S Finney, E Y Kuo *Tetrahedron Lett.* **30** 5747 (1989)
215. L-X Shao, M Shi *Eur. J. Org. Chem.* 426 (2004)
216. D Lee, R D Otte *J. Org. Chem.* **69** 3569 (2004)
217. V Chudasama, J M Ahern, D V Dhokia, R J Fitzmaurice, S Caddick *Chem. Commun.* **47** 3269 (2011)
218. Q Zhang, E Parker, A D Headly, B Ni *Synlett* 2453 (2010)
219. E Zaballos-Garcia, M E González-Rosende, J M Jorda-Gregori, J Sepúlveda-Arques, W B Jennings, D O'Leary, S Twomey *Tetrahedron* **53** 9313 (1997)
220. M T Stone *Org. Lett.* **13** 2326 (2011)
221. L Chu, F-L Qing *Chem. Commun.* **46** 6285 (2010)
222. H S Kim, G Jeong, H C Lee, J H Kim, Y T Park *J. Heterocycl. Chem.* **37** 1277 (2000)
223. J C A Flanagan, L M Dornan, M G McLaughlin, N G McCreanor, M J Cook, M J Muldoon *Green Chem.* **14** 1281 (2012)
224. R B Woodward, K Heusler, J Gosteli, P Naegeli, W Oppolzer, R Ramage, S Ranganathan, H Vorbrüggen *J. Am. Chem. Soc.* **88** 852 (1966)
225. G Ahlgren *Tetrahedron Lett.* **33** 2779 (1974)
226. E Grochowski, T Boleslawska, J Jurczak *Synthesis* 718 (1977)
227. Y Amaoka, S Kamijo, T Hoshikawa *J. Org. Chem.* **77** 9959 (2012)
228. Y Miyake, K Nakajima, Y Nishibayashi *Chem. – Eur. J.* **18** 16473 (2012)
229. I Ruy, A Tani, T Fukuyama, D Ravelli, S Montanaro, M Fagnoni *Org. Lett.* **15** 2554 (2013)
230. D Camp, M Campitelli, G R Hanson, I D Jenkins *J. Am. Chem. Soc.* **134** 16188 (2012)
231. V Nair, S C Mathew, A T Biju, E Suresh *Synthesis* 1078 (2008)
232. V Nair, A T Biju, S C Mathew *Synthesis* 697 (2007)
233. V Nair, A T Biju, K G Abhilash, R S Menon, E Suresh *Org. Lett.* **7** 495 (2005)
234. V Nair, S C Mathew, A T Biju, E Suresh *Tetrahedron Lett.* **48** 9018 (2007)
235. Y Liu, X Chen, M Xue, R Cao, L Liu *Synthesis* 195 (2003)
236. A Papafilippou, M A Terzidis, J Stephanidou-Stephanatou, C A Tsoleridis *Tetrahedron Lett.* **52** 1306 (2011)
237. A Jose, R R Paul, R Mohan, S C Mathew, A T Biju, E Suresh, V Nair *Synthesis* 1829 (2009)
238. D Hong, Y Zhu, X Lin, Y Wang *Tetrahedron* **67** 650 (2011)
239. M Adib, E Sheikhi, A Deljoush *Tetrahedron* **67** 4137 (2011)
240. I Yavari, M Ghazanfarpour-Darjani, Y Solgi, S Ahmadian *Synlett* 1745 (2011)
241. A Alizadeh, S Rostamnia *Synthesis* 1543 (2010)
242. H Huang, Y Wang, Z Chen, W H Hu *Synlett* 2498 (2005)
243. Z Guo, H Huang, Q Fu, W H Hu *Synlett* 2486 (2006)
244. H Huang, W H Hu *Synlett* 1314 (2007)
245. A V Dolzhenko, W-K Chui *J. Heterocycl. Chem.* **43** 95 (2006)