

Di- and polyazides. Synthesis, chemical transformations and practical applications

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The chemistry of organic di- and polyazides has been extensively developed in recent years. Methods for the synthesis of 1,1- and 1,2-diazides are diverse and include stoichiometric, catalytic, photochemical and electrochemical approaches. These organic compounds are highly reactive and are involved in a wide range of reactions, from thermal transformations to click chemistry. Of particular attention are transformations, in which one azido group undergoes intramolecular cyclization, while another azido group remains intact and can participate in further chemical transformations. Tri- and polyazides are investigated as precursors for the production of high-energy materials and the synthesis of high-molecular-weight compounds. This review addresses the methods for the synthesis of organic compounds containing two or more azido groups and their chemical transformations. Aliphatic, aromatic and heteroaromatic diazides are considered. Specific transformations characteristic of geminal and vicinal diazides, which differ from the reactions of monoazides, are described. Examples of the practical application of di-, tri- and polyazides are highlighted. The bibliography includes 355 references.

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1. Introduction

Due to unique properties, azides are widely used in various fields of human activity. For example, the well-known inorganic azide NaN_3 is a gas-generating agent for air bags, since this compound decomposes under thermal or mechanical stress to release nitrogen gas.

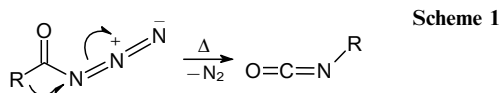
Organic azides have been known since the second half of the 19th century. Thus, in 1864 the German organic chemist Peter Griess^{1,2†} synthesized phenyl azide. More than

25 years later, Theodor Curtius^{3,4} obtained the extremely unstable hydrogen azide and found that acyl azides are capable of rearranging to the corresponding isocyanates; this transformation became known as the Curtius rearrangement (Scheme 1).

However, after that organic azides were almost not studied until the middle of the last century, when a representative series of alkyl, aryl and acyl azides was obtained.^{5,6}

At present, organic azides are widely used not only in the laboratory practice but also in the modern chemical industry. For example, polysulfonyl azides are employed as

† P.Griess. *Philos. Trans. R. Soc. (London)*, **13**, 377 (1864)



blowing agents to create foams and porous rubbers.⁷ The functional azide moiety, despite its potential danger, is present in the molecule of azidothymidine (zidovudine), the first antiretroviral drug used to treat human immunodeficiency syndrome.⁸ Azides are important building blocks in the construction of nitrogen-containing heterocycles, in particular triazoles and tetrazoles, and also serve as substrates in the Staudinger reaction^{9,10} and the Meldal–Sharpless click reaction of copper-catalyzed azide–alkyne cycloaddition (CuAAC).^{11,12} These reactions are widely used in materials science^{13–15} and biochemistry.^{16,17} It should be noted that during the preparation of this review, Morten Meldal and Barry Sharpless were awarded a 2022 Nobel Prize in Chemistry for the development of click chemistry and bioorthogonal chemistry.

The presence of two and more azide groups in one organic molecule leads to the expansion of the pool of available chemical transformations and the diversification of possible applications of di- and polyazides while ensuring that increased instability of such compounds is taken into account. Note that in addition to Banert's monograph,¹⁸ several reviews and monographs have appeared in recent years devoted to azide-containing organic compounds.^{19–23} It is obvious that this trend got a second wind mainly due to the CuAAC reaction discovered at the beginning of the 3rd millennium.^{11,12,24} The aim of the present review is to comprehensively summarize the current state of chemistry of organic di- and polyazides with various mutual arrangement of azide groups. Diazides can be conditionally divided into the following three classes: geminal, vicinal and other azides, in which azide moieties are tethered to each other by at least two carbon atoms.

In this review, much attention is paid to the systematization of key synthetic approaches to geminal and vicinal diazides using a variety of substrates and azide sources. Besides, it summarizes chemical transformations typical of 1,1- and 1,2-diazide organic derivatives, in particular, thermal and photochemical reactions. Also, not only emphasis is given to modern publications but also the relationship of studies of the chemistry of such compounds in the historical development is shown. Therefore, this publication can be considered as a kind of guide to the methods of synthesis and chemical properties of organic diazides.

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Structures of diazides

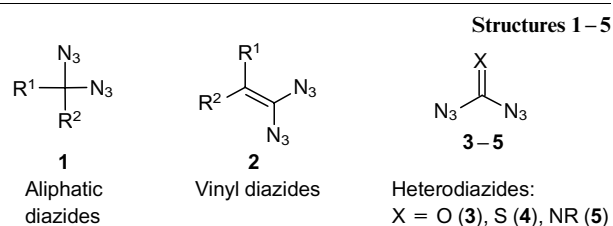


The attention is also paid to the synthesis and chemical transformations of organic compounds bearing three or more azide groups known to date. Such derivatives have been closely studied in recent years as target explosives and coupling agents in macromolecular chemistry.

2. Synthesis and transformations of geminal diazides

In geminal diazides, both azide moieties are attached to the same carbon atom, which can be bonded either to another carbon atom or to a heteroatom. The synthesis method and chemical properties of these compounds depend on which atoms are adjacent to the diazide centre. Structures 1–5 are the most common for geminal, or 1,1-substituted, diazides.

The chemistry of geminal diazides is discussed in depth in a review by Häring and Kirsch.²⁰ The authors focus the readers attention on the extremely explosive nature of such compounds.



2.1. Preparation of aliphatic 1,1-diazides

This Section systematically explores the literature data on the preparation of geminal aliphatic diazides, considers the nucleophilic substitution reactions of a wide range of substrates involving various azide sources and gives examples of diazidation of alcohols, ketones, alkenes, alkynes, *etc.*, in the presence of various oxidants.

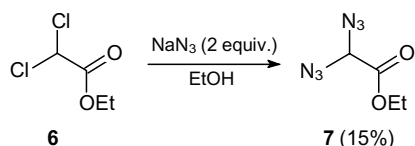
2.1.1. Substitution reactions

Sodium azide is the cheapest and most available source of the azide anion. This is why it is widely used in nucleophilic substitution reactions affording geminal diazides. The synthesis of geminal diazides involving sodium azide was first reported over 100 years ago. Thus, in 1908 Forster *et al.*²⁵ for the first time isolated ethyl 2,2-diazoacetate (7) in a low yield *via* the double substitution of ethyl dichloroacetate (6) in the presence of excess sodium azide (Scheme 2).

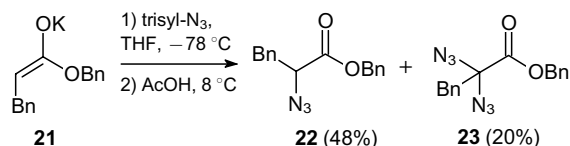
Since then, syntheses of geminal diazides from dihalides using NaN_3 as an azide source have gained popularity, and a large number of such compounds were obtained to date, in particular, α,α -diazido esters,^{2–27} α,α -diazidoketones,²⁸ 2,2-diazidomalonates,²⁹ heterocyclic diazides,^{30–33} *etc.* (e.g., structures 8–15).^{34,35}

Recently, in addition to sodium azide, other reagents were also used for this purpose. An example is azidation polymer 16, which is an Amberlite IR-400 ion exchange

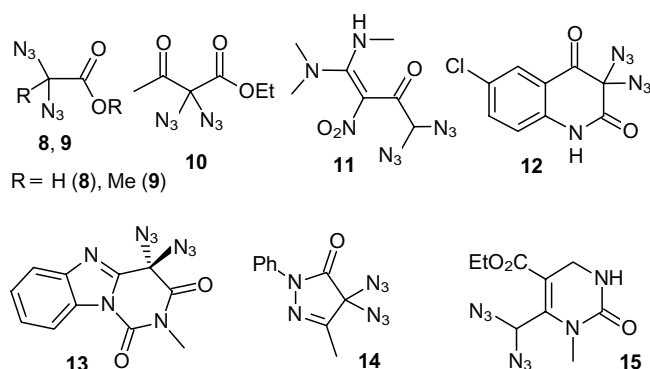
Scheme 2



Scheme 5

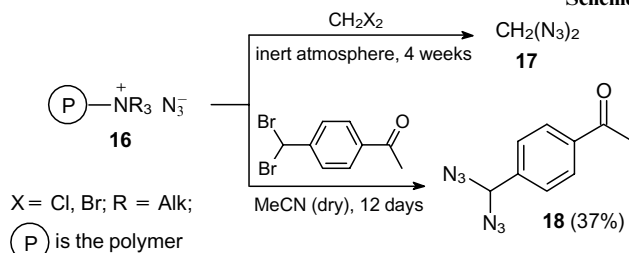


Structures 8–15



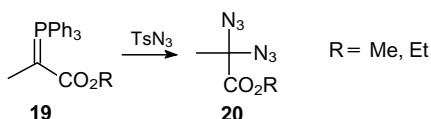
resin with azide ions as counterions (Scheme 3).^{36,37} Such a polymer provides access to low-molecular-weight azides or polyazides, *e.g.*, methyl azide, diazidomethane (**17**), triazidomethane (azidoform) and diazide **18**. Removing the polymeric azidation reagent by filtration gives a solution of a nearly pure reaction product.

Scheme 3



Geminal diazides can also be prepared using an electrophilic source of azide ions, namely, tosyl azide TsN_3 (Ts is *p*-toluenesulfonyl). Thus, in 1972 Sohn *et al.*,²⁶ expecting to obtain diazopropionate on treating phosphorus ylide **19** with diazopropionate, observed the formation of the corresponding diazide **20** (Scheme 4).

Scheme 4

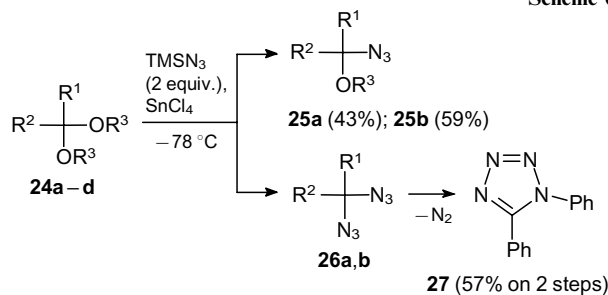


Besides, an attempt was made to perform the direct azidation using hydrocinnamic acid.³⁸ The authors applied the reaction of potassium enolate **21**, generated using potassium hexamethyldisilazide (KHMDs), with 2,4,6-triisopropylbenzenesulfonyl azide (trisyl- N_3) followed by the reaction with acetic acid. Under these conditions, a mixture of monoazide **22** and diazide **23** as a minor product was

obtained (Scheme 5). The reverse addition of enolate **21** to an electrophile improved the yield of azide **22** up to 72%.

Geminal aliphatic diazides are produced by the reactions of acetals and ketals **24a–d** with excess TMSN_3 (TMS is trimethylsilyl) in the presence of strong Lewis acids, *e.g.*, SnCl_4 (Scheme 6).³⁹ In this case, to form diazide, substrate **24** should bear at least one phenyl substituent; otherwise the reaction affords alkoxy azides **25**. Geminal diazide **26a** is produced in 49% yield, whereas its analogue **26b** loses a nitrogen molecule to form tetrazole **27**.

Scheme 6

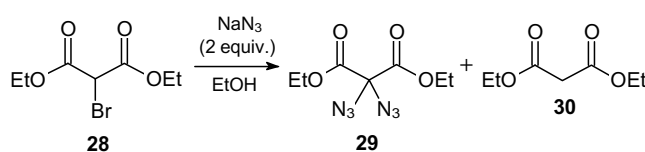


$\text{R}^1 = \text{H}$, $\text{R}^2 = \text{R}^3 = \text{Et}$ (**24a**, **25a**); $\text{R}^1 = \text{R}^2 = \text{Et}$, $\text{R}^3 = \text{Me}$ (**24b**, **25b**);
 $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{R}^3 = \text{Me}$ (**24c**); $\text{R}^1 = \text{R}^2 = \text{Ph}$, $\text{R}^3 = \text{Me}$ (**24d**);
 $\text{R}^1 = \text{Ph}$: $\text{R}^2 = \text{Me}$ (**26a**), Ph (**26b**)

Ketones^{40,41} and aldehydes^{42,43} can also be used as starting materials to prepare geminal diazides; in this case, catalyst SnCl_2 is preferable. This protocol is suitable not as much for aliphatic and aromatic aldehydes, as for their heterocyclic analogues.⁴⁴ Also, it was shown that the addition of a combination of NaN_3 with a crown ether significantly accelerates this process.⁴² It is also known that aldehydes can be directly converted into 1,1-diazides, being treated with NaN_3 in the presence of AlCl_3 or TiCl_4 .^{42,45}

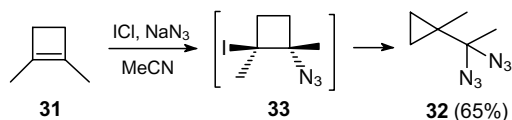
Another approach to 1,1-diazides involves the disproportionation of alkyl 2-bromomalonates **28**, giving the corresponding diazidomalonate **29** (Scheme 7).⁴⁶ However, this method is not very effective, since during the process, the starting compound is partially converted into a by-product, alkyl malonate **30**. Nevertheless, this reaction provides pure 2,2-diazidomalonate **29**, with no traces of monoazide detected.^{47,48}

Scheme 7



When studying the reactivity of 1,2-dimethylcyclobutene (**31**) by treating it with a mixture of excess iodide(I) chloride and sodium azide, O'Hare and Swern⁴⁹ unexpectedly

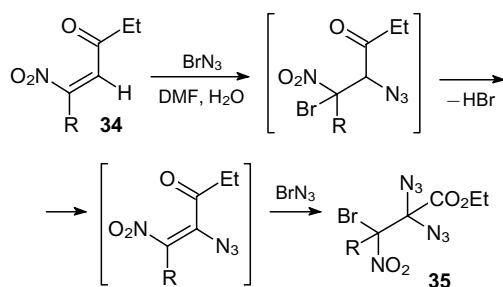
Scheme 8



obtained geminal diazide **32** (Scheme 8). In this case, intermediate **33** undergoes four-membered ring contraction, and both azide moieties occur at the exocyclic carbon atom.

Bromine azide, prepared by the reaction of *N*-bromosuccinimide (NBS) with sodium azide, was used to convert nitro olefins **34** to geminal diazides **35** via the addition–elimination–addition sequence (Scheme 9).⁵⁰

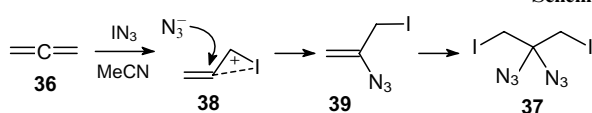
Scheme 9



R = Me (70%), Et (74%), Ph (75%)

Allene (propa-1,2-diene) **36** reacts with iodine azide to give geminal diazide **37** through the intermediate formation of cyclic iodonium ion **38** and monoazide **39** (Scheme 10).⁵¹

Scheme 10



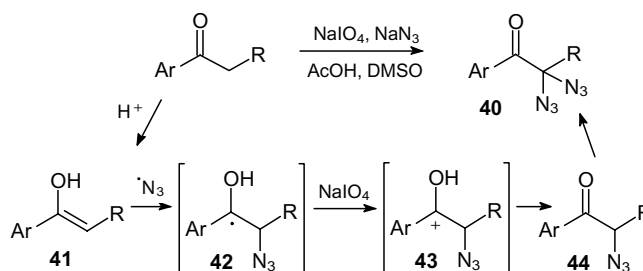
2.1.2. Synthesis of aliphatic 1,1-diazides under oxidizing conditions

Modern techniques enable the direct diazidation of a number of organic compounds, namely, benzyl alcohols,⁵² ketones,^{52,53} diketones, alkenes,⁵³ alkynes,⁵⁴ and also malonates and β -ketoesters,⁵⁵ under oxidizing conditions. In such cases, the reactions afford α -diazidocarbonyl compounds. Hydrogen peroxide,⁵⁶ NaIO_4 , potassium 3-carboxy-4-iodylbenzenesulfonate (IBX- SO_3K) and *N*-iodosuccinimide (NIS) are used as oxidants.

For example, the reaction of both linear and cyclic aryl ketones containing the α -methylene moiety with NaN_3 in the presence of NaIO_4 in a 1 : 4 AcOH–DMSO mixture at 75 °C furnishes α,α -diazidoketones **40** in 93–96% yields (Scheme 11).⁵² However, under these conditions, isobutyrophenone gives solely the α -monoazidation product in 35% yield.

It is believed that the mechanism of this transformation comprises one-electron oxidation of an azide ion, which then adds to enol **41**. The further oxidation of radical **42** generates cation **43**, the abstraction of a proton from which leads to α -azidoketone **44**, which is again involved in the oxidation cycle to provide α,α -diazidoketone **40**. To confirm the formation of intermediate monoazidoketone **44**, tetralone was diazidated⁵² using equimolar amounts of

Scheme 11

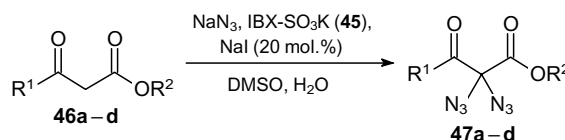


Ar = Ph: R = Me (96%), Bn (94%), 4-MeOC₆H₄CH₂ (95%);
ArC(O)CH₂R = 1-indanone (95%), 1-tetralone (93%)

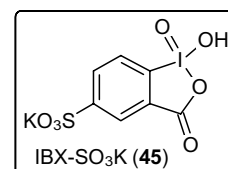
NaN_3 and NaIO_4 to give the corresponding α -diazido-ketone in 28% yield. When individual 2-azido-1-phenylpropan-1-one was diazidated with a mixture of NaIO_4 (1 equiv.) and NaN_3 (2 equiv.), 2,2-diazido-1-phenylpropan-1-one proved to be the only product (92% yield). This fact indicates that the rate of diazidation of monoazidoketone is much higher than that of the starting aryl ketone.

Another approach to 2,2-diazide derivatives using the easy-to-handle and environmentally friendly oxidant IBX- SO_3K (**45**) was developed by Kirsch's research group.^{55,57} This approach is characterized in that it makes available a number of tertiary 2,2-diazido-1,3-dicarbonyl products, which are pretty difficult to prepare using conventional procedures. This method provides an access to diazides starting from 1,3-dicarbonyl compounds, in particular, malonates and β -ketoesters (Scheme 12).

Scheme 12



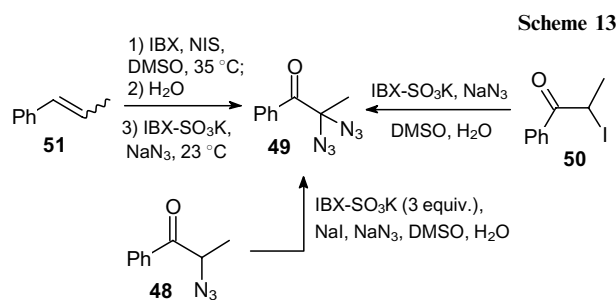
R¹ = OMe, R² = Me (**a**, 50%);
R² = Et: R¹ = Ph (**b**, 77%),
Bu^t (**c**, 79%), 2-Th (**d**, 83%);
Th is thienyl



Being treated with a mixture of IBX- SO_3K (3 equiv.), NaI (0.2 equiv.) and NaN_3 in the DMSO– H_2O system, at room temperature for 10 min, 1,3-dicarbonyl compounds **46a–d**, devoid of an additional substituent in the 2 position, afford rather stable 2,2-diazido-1,3-dicarbonyl compounds **47a–d** in good yields. An advantage of this protocol is the rapid incorporation of an azide-containing moiety, which can further be additionally functionalized via conventional reactions of 1,3-dipolar cycloaddition with terminal alkynes.

Later, this approach was improved and expanded, thereby providing a direct access to geminal diazides bearing one carbonyl moiety from α -azidoketones, α -iodoketones and olefins with an internal double bond (Scheme 13).⁵³

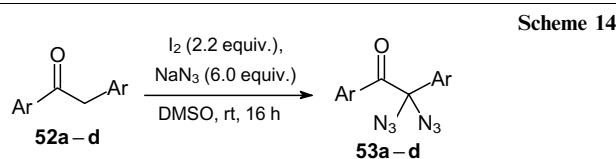
In all cases, NaN_3 was employed as a cheap and easily available azide source, while a combination of IBX- SO_3K with iodides proved to be a perfectly balanced oxidizing



agent. Thus, in the presence of substoichiometric amounts of NaI, 2-azido-1-phenylpropanone **48** was converted into 2,2-diazo-1-phenylpropanone **49** in 82% yield.

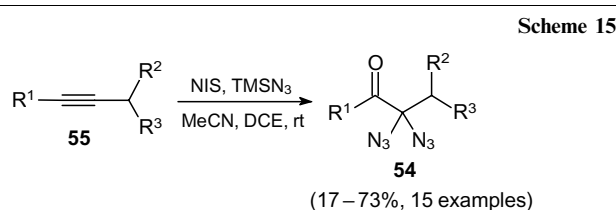
2-Iodo-1-phenylpropanone **50** can be diazidated using IBX-SO₃K and NaN₃ in aqueous DMSO at room temperature in good yield (79%). The synthesis of diazide **49** from an internal olefin, propenylbenzene **51**, comprises primarily the *in situ* transformation of the starting compound into iodomethyl ketone using 2-iodoxybenzoic acid (IBX) and NIS (see Scheme 13).

Diazides **47** can also be prepared from dicarbonyl compounds **46** using an alternative azidation system, I₂-NaN₃, in aqueous DMSO.⁵⁸ This method performed well in diazidating monocarbonyl derivatives **52a–d**. In this way, diazides **53a–d** were produced in high yields (Scheme 14).⁵⁹



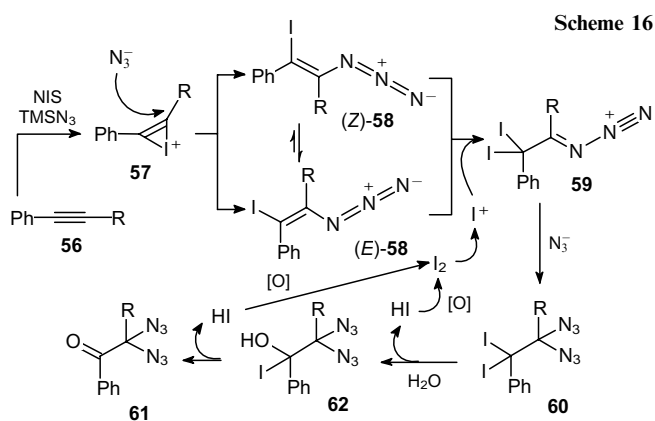
Ar = Ph (**a**, 86%), 4-MeC₆H₄ (**b**, 85%), 4-FC₆H₄ (**c**, 70%), 3-Th (**d**, 89%); rt is room temperature

In 2015, Okamoto *et al.*⁵⁴ developed a rather productive approach to 1,1-diazides **54** based on the reaction of disubstituted arylacetylenes **55** with TMSN₃ as an azide source (Scheme 15). The presence of a minor amount of atmospheric moisture and oxygen contributes to the successful outcome of the reaction, but the authors failed to determine accurately the role of water and oxygen.



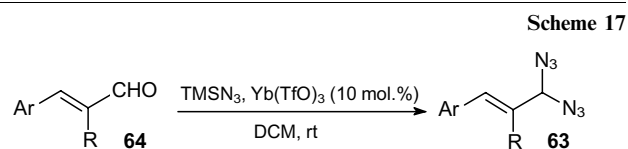
R¹ = Ph, 4-MeC₆H₄, 4-FC₆H₄, 4-F₃CC₆H₄, 3-MeOC₆H₄;
 R² = Alk, OAc, OCO₂Et, OCOC₆H₄Br-4, OBn, OTBS, OBz;
 R³ = H, Alk, Ph; DCE is 1,2-dichloroethane;
 TBS is *tert*-butyldimethylsilyl

On the other hand, an excess of water in the reaction mixture was found to significantly reduce the product yield due to the rapid hydrolysis of TMSN₃. The putative mechanism of the process as exemplified by the transformation of phenylacetylenes **56** is illustrated in Scheme 16.



In the first step, alkyne **56** reacts with NIS and TMSN₃ to form regioselectively, *via* the ring-opening of iodonium intermediate **57**, a mixture of *E* and *Z* isomers of alkene **58**. It was found^{60–62} that the regioselectivity of the addition of IN₃ to arylalkyne is opposite to that predicted from the electronic effect and that the addition of IN₃ results in the formation of two stereoisomers. Using ¹H NMR spectroscopy, it was shown that the reaction between NIS and TMSN₃ affords iodine azide IN₃. The iodination of alkene **58** generates intermediate **59**, and its subsequent reaction with the azide anion gives diazide **60**, which is then hydrolyzed by atmospheric moisture to afford diazidoketone **61** *via* the formation of intermediate **62**. In this case, oxygen oxidizes HI to I₂, which binds to the remaining compound **58** in the form of I⁺.

Particularly noteworthy is the recently developed synthetic approach to α,β -unsaturated geminal diazides **63** derived from unsaturated aldehydes **64** using TMSN₃ as the azide source and Yb(TfO)₃ as the catalyst (Scheme 17).⁶³ This reaction proceeds in a one-step fashion under mild conditions to provide the product in moderate yield.



DCM is dichloromethane

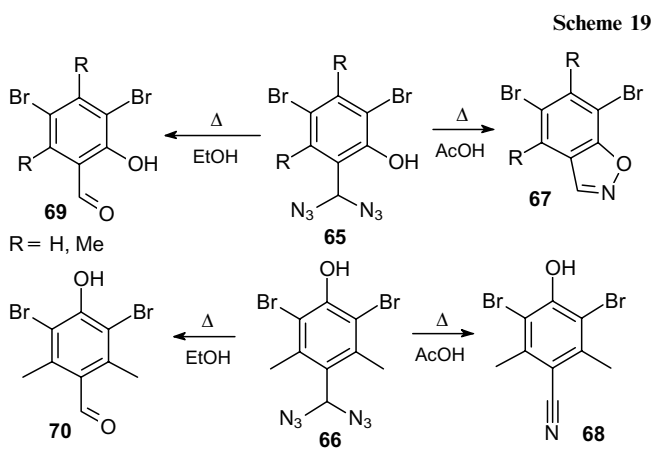
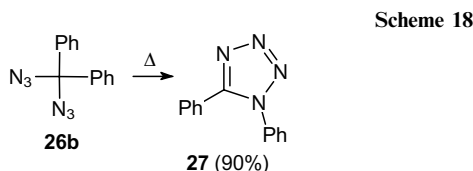
2.2. Reactions of geminal aliphatic diazides

This Section presents the fundamental reactions of geminal diazides, including thermolysis and photolysis, and also several examples of intermolecular reactions, most of which afford nitrogen-containing heterocycles of unique classes.

2.2.1. Thermal and photochemical reactions

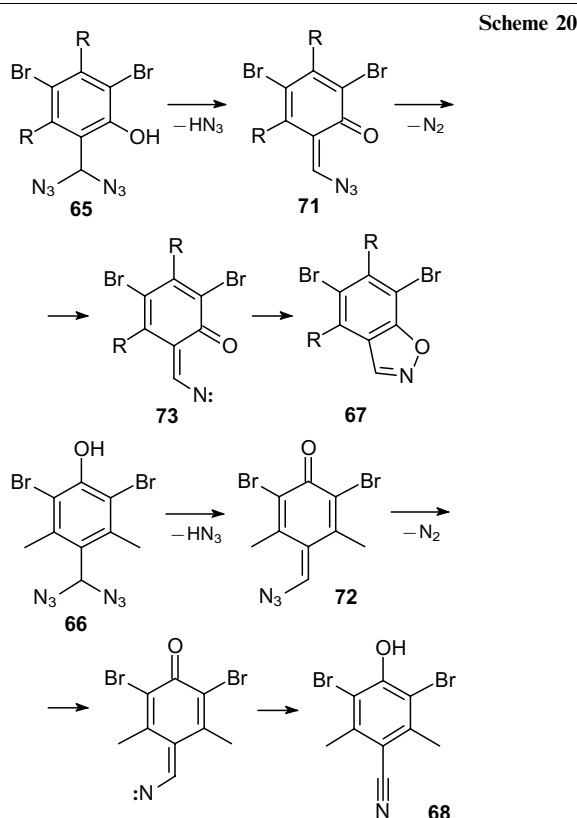
In the early 20th century, it was found that the thermal decomposition of diazodiphenylmethane **26b** gives tetrazone **27** (Scheme 18).^{64, 65}

However, when studying the thermal reactions of *ortho*-(**65**) and *para*-hydroxy-disubstituted (**66**) benzyl diazides, Lindemann and Mühlhaus⁶⁶ revealed the formation of benzisoxazoles **67** and benzonitrile **68**, respectively (Scheme 19). Besides, when carrying out the reaction in ethanol, benzaldehydes **69** and **70** were obtained. The formation of these compounds is probably attributed to



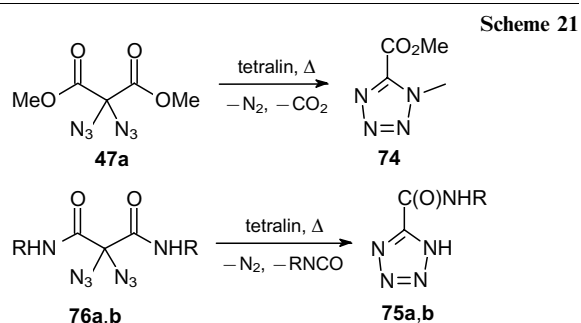
the hydrolysis of diazides due to the presence of water in the solvent.

The mechanisms of formation of benzisoxazoles **67** and benzonitrile **68** are presented in Scheme 20. One might note the similarity of these mechanisms: in both cases, HN_3 is first eliminated to afford quinoid derivative **71** or **72** followed by the loss of a nitrogen molecule. The difference occurs only in the last step. In the presence of the *ortho*-hydroxy group, intermediates **73** are stabilized *via* the formation of a new isoxazole ring. When the hydroxy



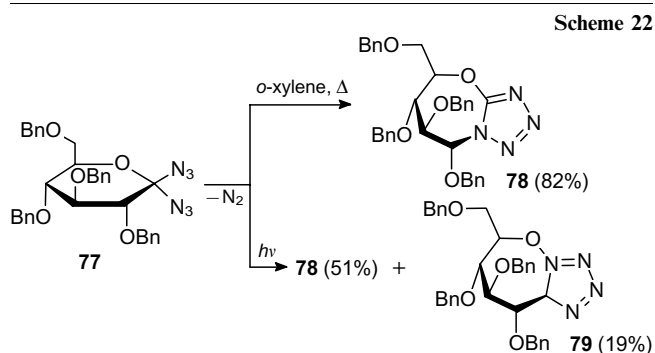
group is in the *para* position, only the diazidomethyl moiety undergoes transformations, without affecting the hydroxy functionality. A number of more recent publications^{42, 45, 67–69} also reported the synthesis of benzonitriles using conventional reagents, such as NaN_3 or TNSN_3 . In these reactions, benzyl diazides are often formed *in situ* as intermediates.

Thermal decomposition of geminal diazides also affords interesting organic compounds. Thus, tetrazoles **74** and **75** can be obtained by heating dimethyl 2,2-diazidomalonate **47a** and diamides **76a,b**, respectively, in nonpolar solvents, *e.g.*, tetralin (Scheme 21).⁴⁸

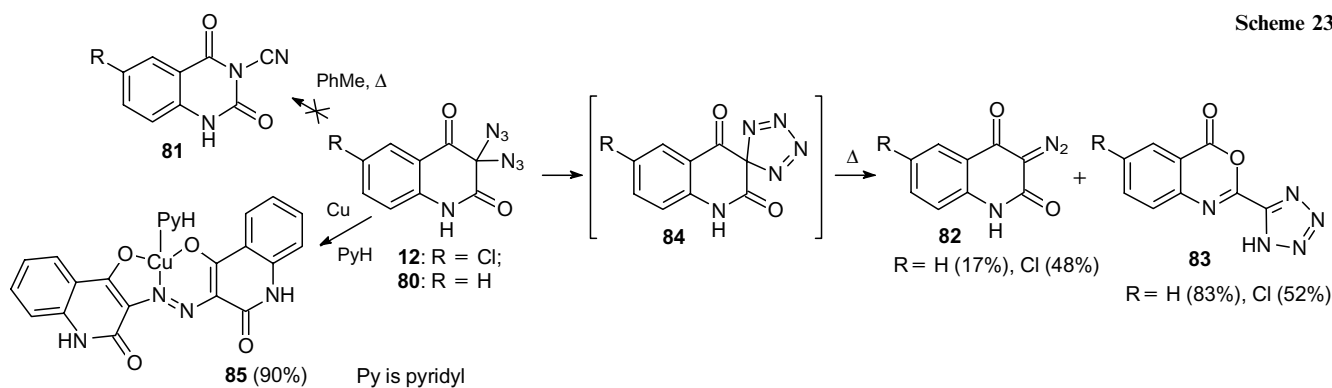


R = H (**a**, 94%), Me (**b**, 90%)

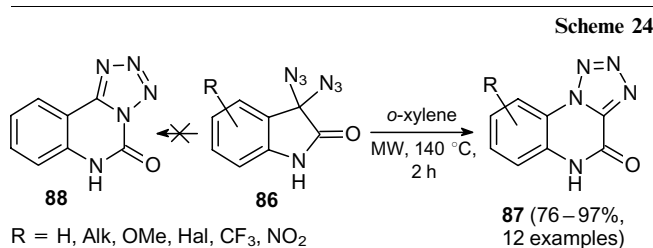
Thermal decomposition of glucopyranoside *gem*-diazide **77** produces tetrazole **78** in high yield. Meanwhile, the photochemical decomposition of diazide **77** gives a mixture of tetrazoles **78** and **79** (Scheme 22).⁷⁰ Probably, tetrazole **79** is formed through the generation of intermediate azido-nitrene followed by its insertion across the carbon–oxygen bond.



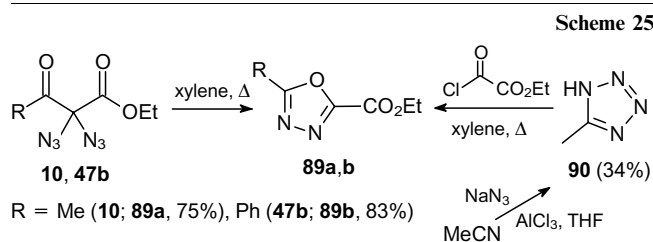
When studying the thermal decomposition of 3,3-diazido-2,4-dioxoquinolines **12** and **80**, Landen and Moore³⁰ suggested the formation of *N*-cyano derivatives **81**. However, a careful study of the by-product structures indicated the formation of isomeric 3-diazoquinoline-2,4-diones **82**, which have already been known for a long time and used to prepare azo dyes⁷¹ and their complexes with copper⁷² (Scheme 23). In addition to diazo compounds **82**, the authors also observed the formation of tetrazoles **83**. It was suggested that products **82** and **83** are formed *via* the common intermediate, spirocyclic tetrazole **84**. Besides, in refluxing pyridine in the presence of copper, 3,3-diazido-2,4-dioxoquinoline **80** gave coordination compound **85** in high yield.



Microwave irradiation (MW) enables the cyclization of geminal diazides **86** to tetrazole derivatives **87** in high yields (Scheme 24). The same method was used to produce tetrazoles from the open-chain diazidoketones. However, under these conditions, no isomeric tetrazoles **88** are formed.⁷³

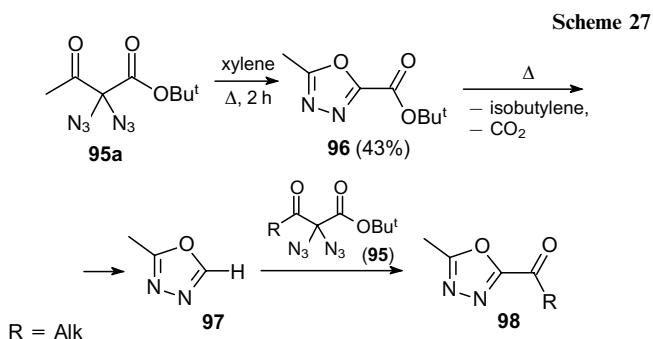
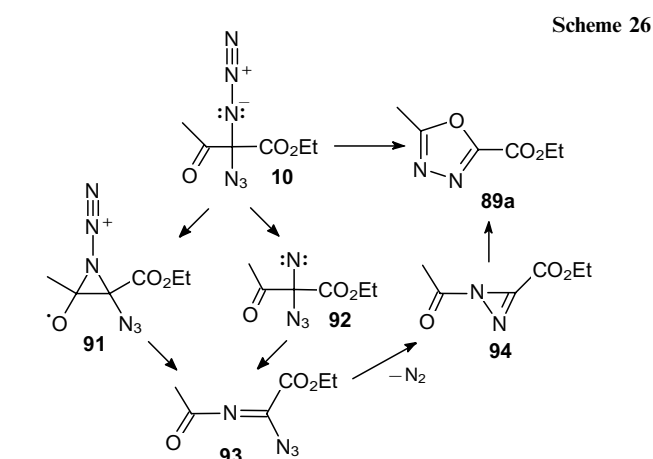


Ogilvie and Rank⁷⁴ pioneered in the synthesis of 1,3,4-oxadiazoles **89a,b** via heating α,α -diazido- β -ketoesters **10** and **47b** (Scheme 25). The structure of product **89a** was additionally confirmed by the independent synthesis from 5-methyltetrazole (**90**).



The authors believe that diazido compound **10** converts to aziridine **91** or loses a nitrogen molecule to afford nitrene **92**. The ring opening or subsequent migration of the acyl group to the nitrogen atom leads to azido azomethine intermediate **93**. The loss of a second nitrogen molecule directly from azido azomethine **93** gives diazirine **94**, which is finally rearranged into 2,5-disubstituted 1,3,4-oxadiazole **89a** (Scheme 26).

Almost 30 years later, Erhardt, Mohr and Kirsch⁷⁵ continued to study this reaction and significantly expanded the scope of the resulting 1,3,4-oxadiazoles. It was also demonstrated that in the case of *tert*-butyl-substituted esters (e.g., compound **95a**), further heating of product **96** led to the removal of the ester functionality (intermediate **97**) accompanied by the possible transfer of a new acyl moiety from ester **95a** giving compounds **98** (Scheme 27).

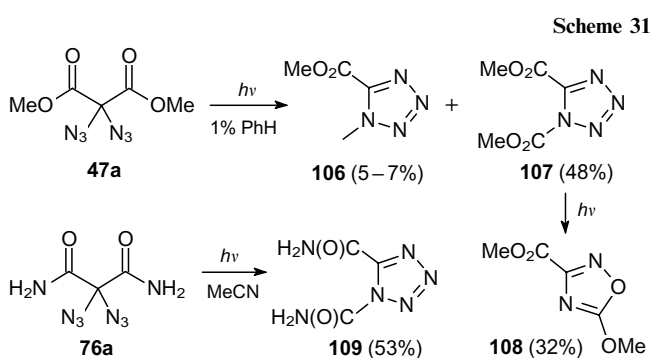
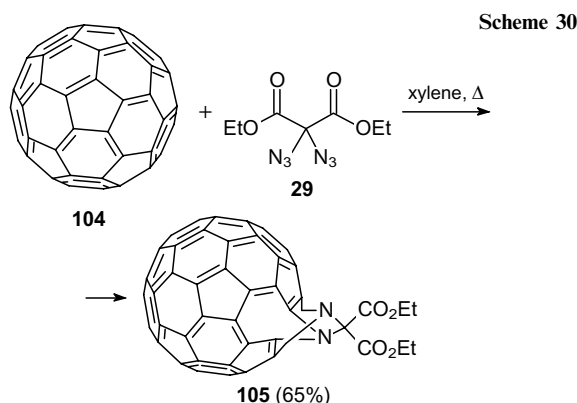
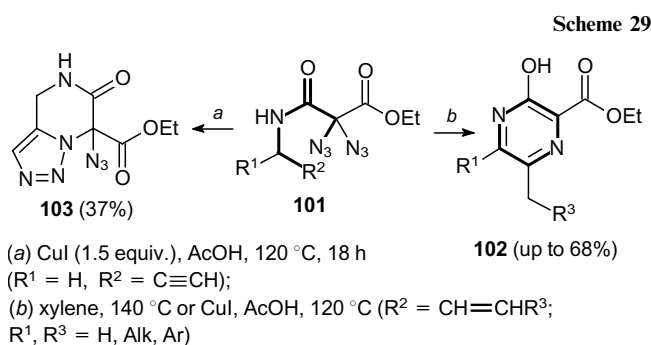
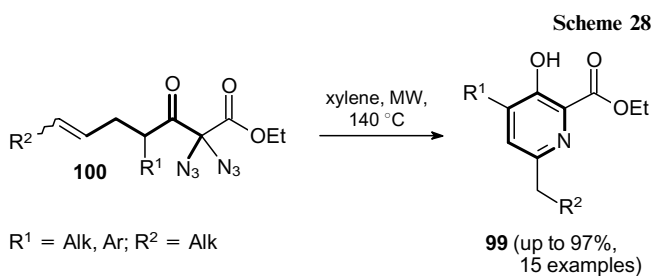


A similar approach can be applied to the synthesis of pyridine derivatives **99** from 1,1-diazides **100** under microwave irradiation (Scheme 28).⁷⁶

Heating of diazides **101** induces the cyclization to pyrazines **102** or the intramolecular cyclization onto one azido moiety leading to azidotriazole **103** (Scheme 29).⁷⁷

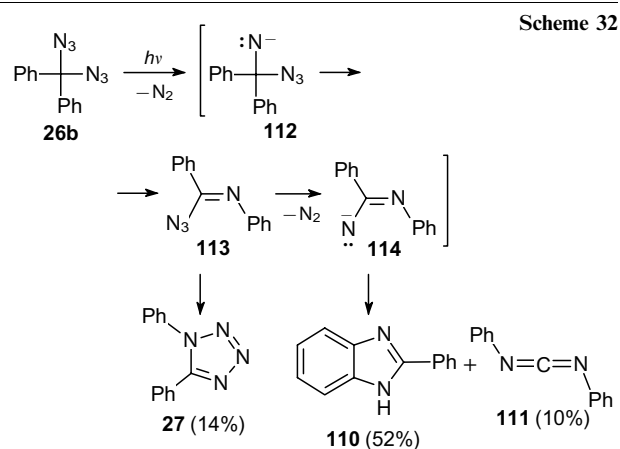
Geminal diazides can be used as nitrene precursors. For example, C₆₀ fullerene (**104**) was refluxed in xylene with ethyl 2,2-diazidomalonate (**29**) to produce functionalized bridged fulleroid **105** (Scheme 30).⁷⁸

Over half a century ago, Moriarty *et al.*⁴⁷ studied the photolysis of three geminal diazides, namely, methyl 2,2-diazidomalonate (**47a**), 2,2-diazidomalonimide (**76a**) and diazidodiphenylmethane (**26b**). As is seen in Scheme 31, the photolysis of diazides **47a**, **76a** produces mixtures of different products **106–109**, suggesting the existence of several reaction pathways.



The authors presented some mechanistic aspects⁷⁹ including the formation of nitrene intermediates, which was confirmed by EPR spectroscopy. However, the final mechanism that explains all observations on photolysis of diazides, is still unclear. From a synthetic point of view, tetrazole **107** is the major product that is formed upon irradiation of compound **47a**. Its further irradiation results in a loss of a nitrogen molecule to give methyl 5-methoxy-1,2,4-oxadiazole-3-carboxylate **108**, while irradiation of 2,2-diazidomalonamide **76a** furnishes tetrazole **109**.

Meanwhile, diazidodiphenylmethane (**26b**) shows a completely different distribution of products **27**, **110** and **111** (Scheme 32), which implies the reaction to proceed *via* intermediates **112**–**114**.

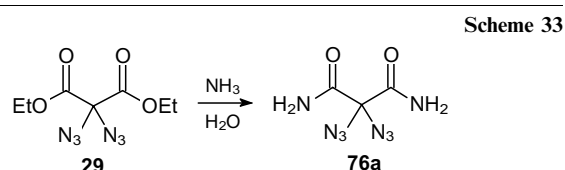


More recent studies of the photochemistry of geminal benzyl azides using density functional theory (DFT) calculations and isotope labeling experiments also supported the hypothesis that there is more than one reaction pathway.³⁷

Harter *et al.*⁸⁰ synthesized salts of 2,2-diazidomalonate containing sodium, potassium, ammonium and guanidinium counterions. These compounds were tested for sensitivity towards impact, friction and electrostatic discharge in comparison with trinitrotoluene. It turned out that some of them are superior in terms of velocity of detonation to trinitrotoluene. Also, the toxicity of these compounds to aquatic organisms was studied using the bioluminescent marine bacterium *Vibrio fischeri*.⁸⁰

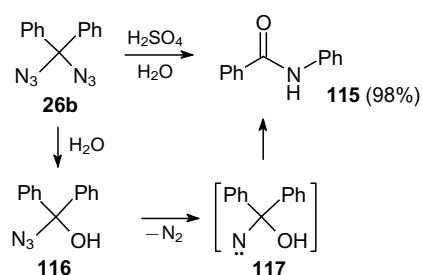
2.2.2. Intermolecular reactions

The conversion of geminal diazide **29** to 2,2-diazidomalonamide (**76a**) in the presence of ammonia has been known for more than 100 years (Scheme 33).²⁹ Azide moieties are not directly involved in this reaction but appear to exert a strong activating effect since the formation of the corresponding amide from unsubstituted diethyl malonate (**30**) is much slower.



In 1931, the transformation of diazidodiphenylmethane **26b** into *N*-phenylbenzamide **115** under the action of strong acids was reported.⁶⁵ The hydrolysis of diazide **26b** gives intermediate **116**, which loses a nitrogen molecule to afford nitrene **117**. The subsequent rearrangement of this intermediate yields *N*-phenylbenzamide **115** (Scheme 34).

It should be noted that because of the issues with the commercial availability and storage of *gem*-diazides, studies of the reactivity of such compounds were scarce for a long time in contrast to the studies of more stable monoazides. Nevertheless, significant progress has been made in this area over the past 5 years. The reaction between aromatic



Scheme 34

aldehydes with TMSN_3 was used to produce *gem*-diazides **118**, and their reactions with heterocyclic carbene **119** and triphenylphosphine giving products **120** and **121**, respectively, were described (Scheme 35).⁸¹

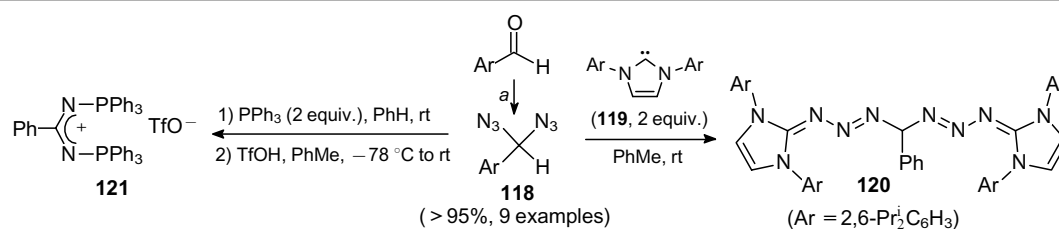
Recently, oxidative geminal diazidofunctionalization of alkynes was accomplished, in which tetra-*n*-butylammonium bromide (TBAB) was a precursor in the *in situ* preparation of tetra-*n*-butylammonium azide.⁸² Besides, based on the reaction of anilines **122** with acetylenedicarboxylates **123**, the cycloamination strategy was first demonstrated yielding quinoxalines **124** (Scheme 36). The reaction sequence includes the formation of compounds

125 and **126**. From the latter compound, product **127** was also obtained.

Considerable advances in intermolecular reactions of geminal diazides were achieved by Kirsch and co-workers⁸³ (Scheme 37). Azido moieties in compound **29** can be hydrogenated over Pd/C to produce amines **128**, in which an amino functionality is located between two carbonyls.⁸⁴ This reaction can be applied to a variety of geminal dicarbonyl diazides and is an alternative to the conventional synthesis of such amines *via* the reduction of the appropriate oximes.⁸⁵

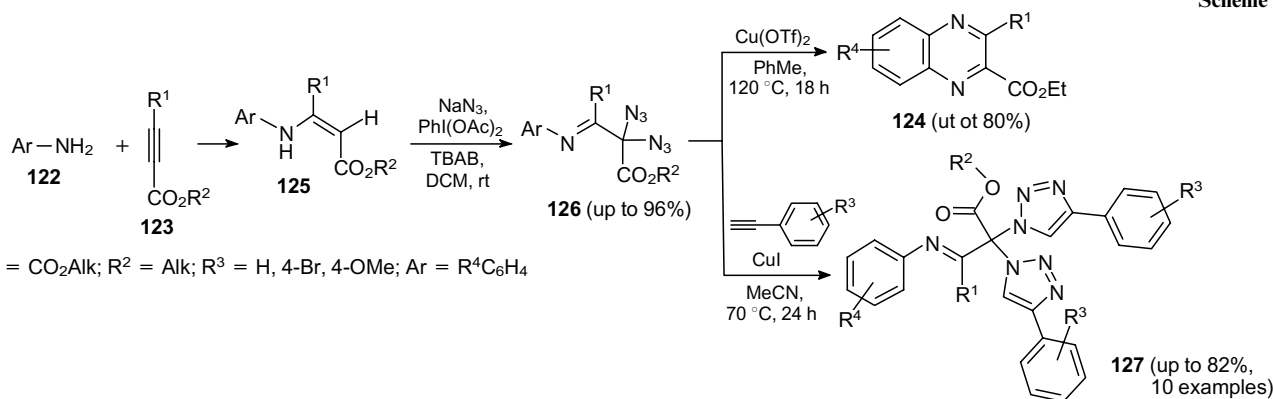
Diazide **29** undergoes the [3 + 2]-cycloaddition with terminal acetylenes to give bis(triazoles) **129**.^{53, 86} The reaction of this diazides with primary amines enables the preparation of diamide derivatives of geminal 2,2-diazides **76**,^{58, 59} which in turn can react with alkynes to afford bis(triazoles) **130**⁸⁷ and also react with alcohols accompanied by the substitution of one azido group to form monoazides **131**. This transformation involving thiols leads to compounds **132**.⁸⁸ Finally, diazides **76** can be transformed into imines **133** using primary amines as nucleophiles.⁷⁹

It is remarkable that the hydrogenation of substrate **10**, in contrast to the hydrogenation of diazide **29** under similar



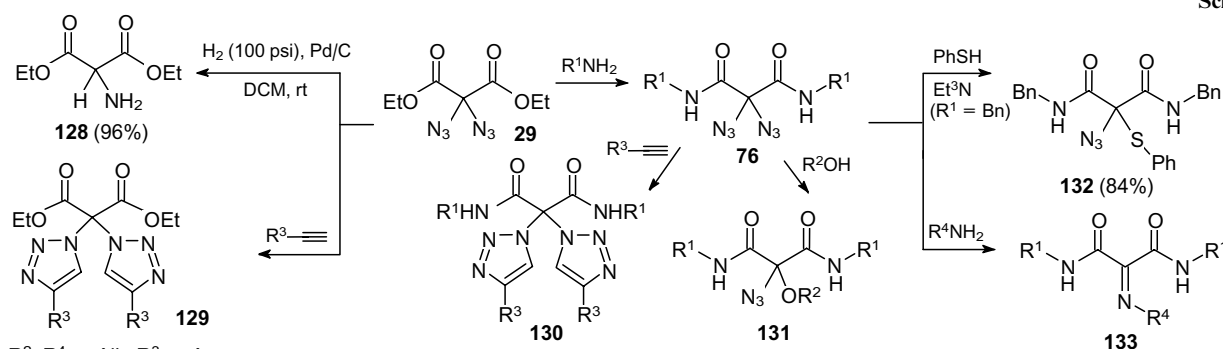
Scheme 35

(a) TMSN_3 (2 equiv.), TfOH (0.1 mol.%), C_6D_6 , rt; Tf is trifluoromethanesulfonyl (triflyl)



Scheme 36

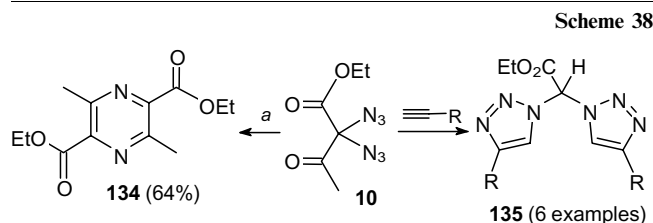
$\text{R}^1 = \text{CO}_2\text{Alk}$; $\text{R}^2 = \text{Alk}$; $\text{R}^3 = \text{H}, 4\text{-Br}, 4\text{-OMe}$; $\text{Ar} = \text{R}^4\text{C}_6\text{H}_4$



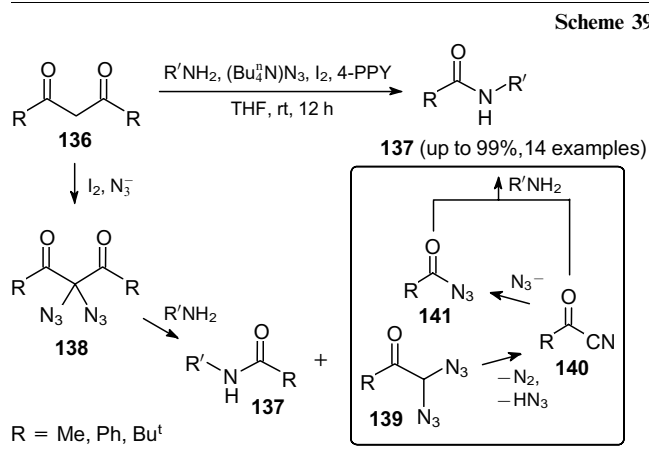
Scheme 37

$\text{R}^1, \text{R}^2, \text{R}^4 = \text{Alk}$; $\text{R}^3 = \text{Ar}$

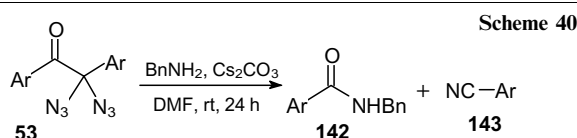
conditions, leads to a kind of dimerization of diazide to furnish pyrazine **134** in moderate yield.⁷⁹ Diazide **10** can also undergo the [3 + 2]-cycloaddition reaction catalyzed by the conventional CuSO₄–sodium ascorbate system to give geminal bis(triazoles) **135** in yields up to 91% (Scheme 38).⁸⁹



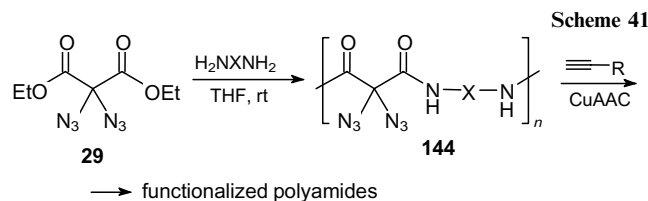
Kirsch and co-workers^{58,90,91} also developed a method for the oxidative cleavage of 1,3-diketones **136** to amides **137** upon the treatment with (Bu^tN)₃ and iodine in the presence of an amine at room temperature. In most cases, 4-pyrrolidinopyridine (4-PPY) was used as the additive. According to the preliminary mechanistic studies, following the diazidation of the enol form, diazide **138** reacts with the amine through the attack on the carbonyl group, resulting in the cleavage of diazide **139**, which also gives the final product *via* the formation of intermediates **140** and **141**, (Scheme 39).



It was subsequently demonstrated that diazidoketones **53** can undergo a controlled fragmentation when treated with primary amines in the presence of caesium carbonate, thereby providing access to the corresponding amides **142** and benzonitriles **143** (Scheme 40).⁵⁹



Diazidomalonate **29** was used as a monomer in the synthesis of polyamides **144** containing geminal diazido units within the polymer backbone. The post-modification of such diazido units using the CuAAC reactions allows for the design of highly functionalized polymeric structures



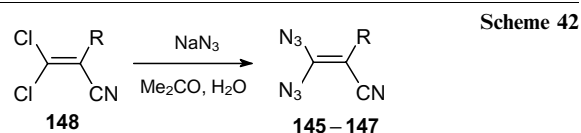
R = Ph, CH₂C(O)OAlk, CH₂OAlk; X = (CH₂)_n (n = 5, 6),
(CH₂CH₂O)₂, CH₂-*p*-C₆H₄-CH₂

(Scheme 41).⁸⁷ This reaction and some other transformation typical of geminal aliphatic diazides, are presented in a mini-review by Çelik and Kirsch.¹⁹

2.3. Geminal vinyl diazides

2.3.1. Synthesis of vinyl diazides

A significant number of publications addressing the synthesis of geminal vinyl diazides appeared in the 1980s.^{92–95} Diazides **145–147** are generally prepared by the simple replacement of chlorine atoms in compounds **148** with sodium azide in an acetone–water mixture at a temperature below 0 °C. The resulting methyl 3,3-diaziido-2-cyanoacrylate (**145**) and ethyl 3,3-diaziido-2-cyanoacrylate (**146**) are yellow crystalline compounds, stable in solution at 15 °C within several days but slowly decomposing at room temperature. Compounds **145** and **146** spontaneously detonate at 70 °C and 50 °C, respectively. 2-(Diazidomethylene)malononitrile **147** was described as an orange oily compound (Scheme 42). Diazides **145** and **146** were isolated by filtration, while in the case of product **147**, the water-insoluble oily product was separated.



R = CO₂Me (**145**, 86%), CO₂Et (**146**, 70%), CN (**147**)

Research of the scientific group led by V.G.Nenajdenko^{96,97} also included the synthesis of geminal vinyl diazides from the appropriate dihalo derivatives using sodium azide as the azide source. These works will be considered below in the Section on the reactivity of such diazides.

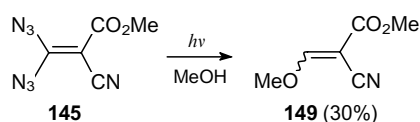
2.3.2. Transformations of vinyl diazides

Transformations involving geminal vinyl diazides are quite diverse.⁹⁸ The reactions characteristic of such compounds can be divided into three main types. The first type includes the monomolecular decomposition, which can be both thermal and photochemical. Scheme 43 exemplifies a photochemical reaction, which occurs upon photoirradiation of a methanolic solution of methyl 3,3-diaziido-2-cyanoacrylate (**145**). This reaction affords methyl 3-methoxy-2-cyanoacrylate (**149**).^{99–101}

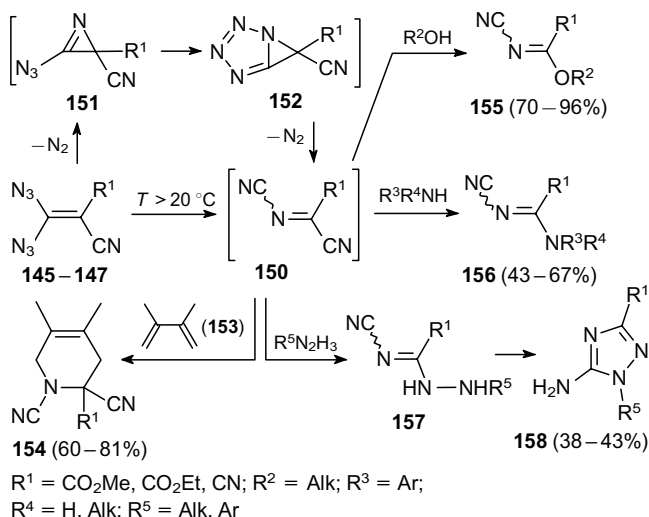
Compared to the photochemical decomposition, which has not yet been studied in detail, thermal reactions of geminal vinyl diazides were investigated more extensively (Scheme 44).^{102–106}

Electrophilic doubly acceptor-substituted *N*-cyanoimines **150** are key intermediates in such transformations.¹⁰⁷ At temperatures > 20 °C, vinyl azides **145–147** lose one

Scheme 43



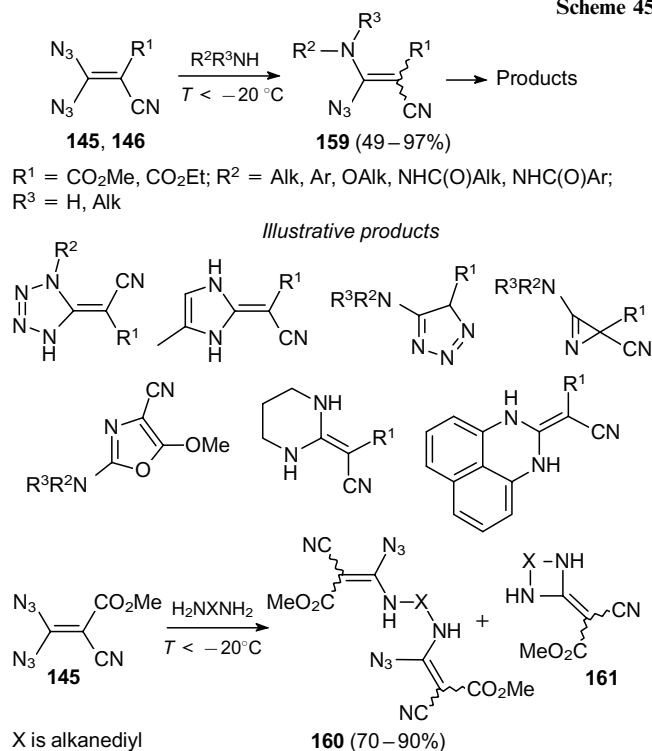
Scheme 44



nitrogen molecule to form azidoazirines **151** that spontaneously cyclize to tetrazoles **152**.¹⁰⁶ After releasing a second nitrogen molecule and subsequent rearrangement, the latter compounds give *N*-cyanoimines **150**. Such intermediates were characterized only in solution^{94,106} since all attempts to isolate them in an individual state ended in polymerization.^{106,107} The existence of these intermediates was also confirmed by their cycloaddition to 2,3-dimethylbuta-1,3-diene (**153**) to afford Diels–Alder products **154**.^{92–94,107,108} In the presence of alcohols^{102,103,107,108} or amines,^{102–106} *N*-cyanoimines **150** are instantly attacked at the electrophilic carbon atom to produce, after the release of hydrogen cyanide, the corresponding compounds **155** or **156** in good yields. The reaction of *N*-cyanoimines **150** with hydrazines furnishes compound **157**, the product of the formal substitution of the cyanide moiety. A further cyclization yields 1,2,4-triazoles **158**.¹⁰⁸

The nucleophilic substitution of an azide moiety is another fundamental reaction of geminal vinyl diazides **145** and **146** to produce intermediates **159** (Scheme 45). Formally, this process should be considered as an addition followed by elimination of hydrazoic acid. Due to thermal instability of the starting compound, this reaction should be carried out at a temperature below $-20\text{ }^\circ\text{C}$. Otherwise, *N*-cyanoimine will be generated before the intermolecular reaction occurs. Primary^{95,106,108,109} and secondary amines,^{103,106} diamines^{104,106} and hydrazines⁹⁵ were tested as nucleophiles. In the case of diamines, the substitution occurs either in two different molecules of diazide **145** to yield bis(vinyl azides) **160**,^{104,106,108} or in the same molecule to afford cyclic products **161**.¹⁰⁴ In the reaction of simple amines with geminal vinyl azides, one azide functionality is substituted to give the corresponding vinyl azide **159**. Further transformations of vinyl azide **159** provide access to a variety of nitrogen-containing heterocycles such as tetrazolylienes,⁹⁵ imidazolylienes,¹⁰⁹ oxazoles,^{104,109} 1,2,3-triazoles,¹⁰⁸ azirines, *etc.* The reaction outcome

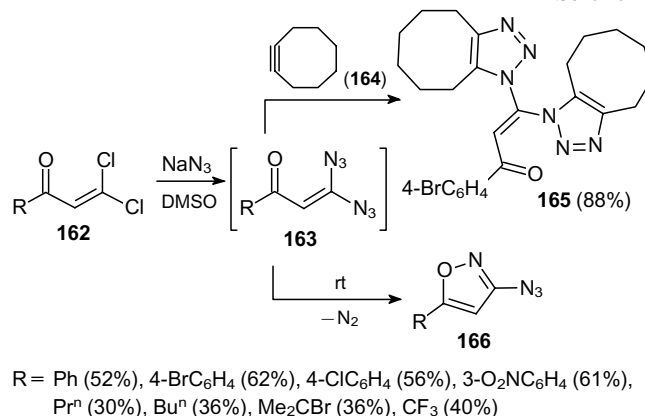
Scheme 45



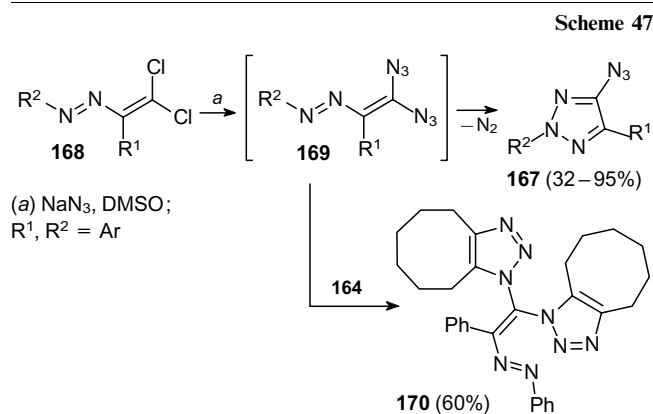
strongly depends on the substitution pattern in vinyl azide **159** and reaction conditions.

Noteworthy are the reactions of geminal vinyl diazides discovered in recent years, in which one azido group is involved in the intramolecular cyclization with any functional group, while another azide group remains intact and can be involved in further transformations of the newly formed cyclic azide.^{96,97} Thus, the reaction between geminal dichlorovinyl ketones **162** and sodium azide was studied.⁹⁶ Using NMR spectroscopy and quantum chemical calculations, it was shown that this process produces the corresponding geminal 3,3-diazoenones **163** (Scheme 46). These highly reactive compounds can be captured by cyclooctyne (**164**) to give bis(triazoles) **165** in high yields. In the absence of the capturing agent, 3,3-diazoenones **163** spontaneously cyclize into 3-azidoisoxazoles **166**. According to calculations, the intramolecular cyclization proceeds through the nucleophilic attack of the carbonyl oxygen on the nitrogen atom with the release of a N_2 molecule.

Scheme 46



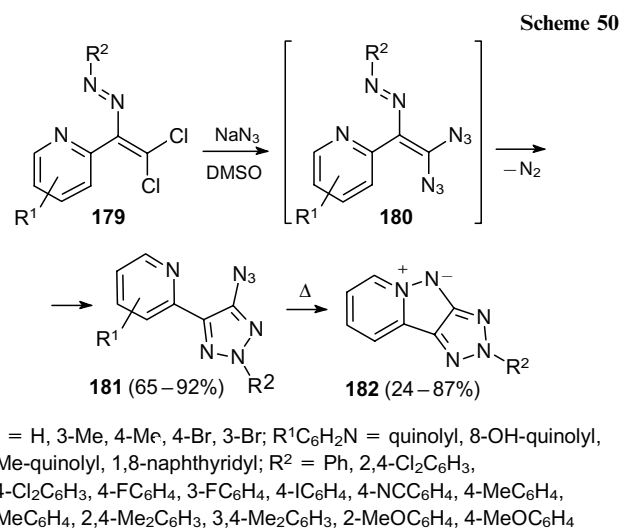
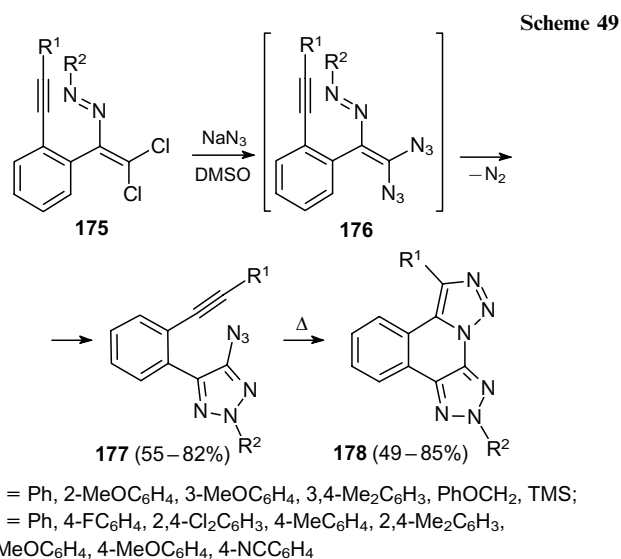
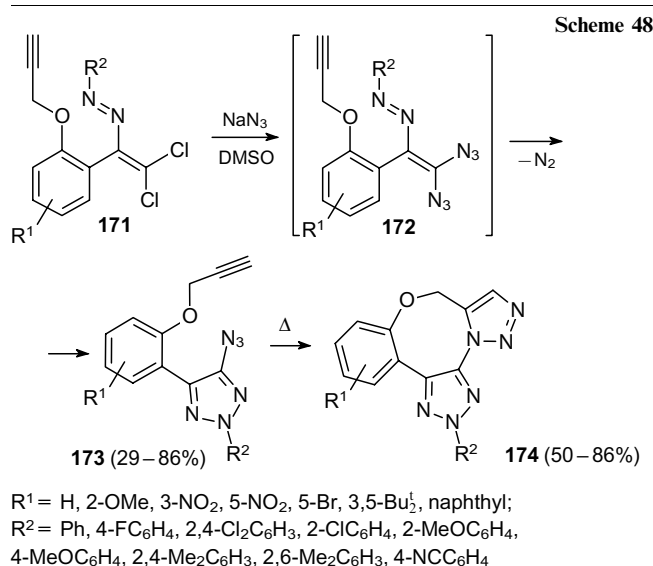
Tsyrenova and Nenajdenko¹¹⁰ developed an effective method for the synthesis of 4-azido-1,2,3-triazoles **167** based on the treatment of dichlorodiazadienes **168** with an excess of NaN_3 (Scheme 47). Geminal diazide **169** is an intermediate product of this transformation; its formation was confirmed by the reaction of dichlorodiazadiene with NaN_3 in the presence of cyclooctyne (**164**), which produced bis(triazole) derivative **170**.



The introduction of an acetylene moiety in the *ortho* position of the aryl substituent at the C(3) carbon atom of dichlorodiazadienes **171** and their subsequent treatment with sodium azide lead first to diazides **172** and then to the corresponding acetylene-substituted 4-azido-1,2,3-triazoles **173**, which can be transformed into various fused heterocyclic systems.¹¹⁰ In particular, the thermal intramolecular cyclization of *o*-propargyloxy-substituted 4-azido-1,2,3-triazoles **173** gives rise to a variety of oxazocine derivatives **174** in good yields (Scheme 48).

Dichlorodiazadienes **175**, via the formation of vinyl diazides **176**, also gave *ortho*-alkynyl-substituted 4-azido-1,2,3-triazoles **177**, which were transformed into isoquinoline derivatives **178** when heated in toluene (Scheme 49).¹¹¹

Finally, under similar conditions, pyridine-containing dichlorodiazadienes **179** gave 2-pyridine-substituted diazides **180** and 4-azido-1,2,3-triazoles **181**, which, when heated in *o*-xylene, furnished pyridopyrazole derivatives **182** with a highly polar $\text{N}^+ - \text{N}^-$ bond (Scheme 50).¹¹²



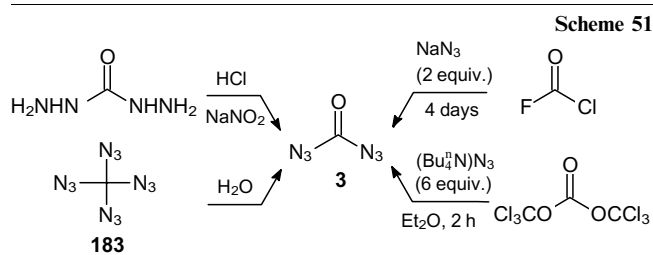
2.4. Geminal heterodiazides

2.4.1. Diazidophosgene

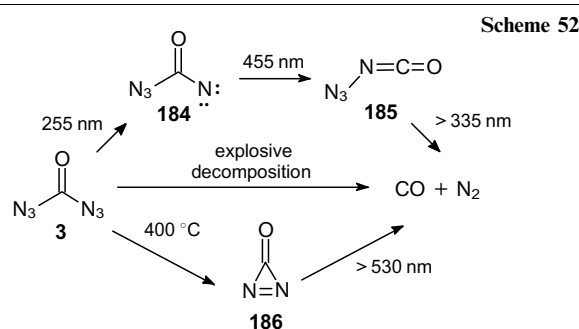
Recently, a large number of notable polyazides of Groups 15 (P, As, Sb)^{113–116} and 16 (Se, Te)^{117–122} of the Periodic table were synthesized and structurally characterized. As for carbon, Group 14 element, a few organic mono- and diazides are well known, and some of them are quite stable at room temperature and even commercially available. Meanwhile, one of the simplest carbon diazides, carbonyl diazide (or diazidophosgene, $\text{OC}(\text{N}_3)_2$ (**3**)), was poorly explored. Thus, the synthesis of this compound and its use *in situ* were reported in a few papers.^{123–125} In 2007, diazide **3** was mentioned in a publication¹²⁶ as a hydrolysis product of diazidomethane, as evidenced by ^{13}C and ^{15}N NMR spectroscopy, but the authors did not isolate it in the pure form.

Three years later, a safe method for the synthesis and precautions for handling carbonyl diazide $\text{OC}(\text{N}_3)_2$ as a pure substance in small quantities were described.¹²⁷ The physical properties of this compound were investigated and it was fully characterized by IR (gas-phase, Ar matrix) and Raman (solid-state) spectroscopy and X-ray crystallography. Carbonyl diazide was prepared by reacting NaN_3 with an excess of $\text{FC}(\text{O})\text{Cl}$ in a sealed glass ampoule at

room temperature for 4 days. Volatile products from three batches were collected and separated by repeated condensation at different temperatures. Thus, product **3** was trapped at $-60\text{ }^{\circ}\text{C}$ as a white solid. More volatile intermediate azide $\text{FC}(\text{O})\text{N}_3$ was trapped at $-100\text{ }^{\circ}\text{C}$, while unreacted $\text{FC}(\text{O})\text{Cl}$ was trapped at $-196\text{ }^{\circ}\text{C}$. Later, various routes for the generation of carbonyl diazide were described,¹²⁸ including that from tetraazidomethane (**183**) (Scheme 51) but none of these reactions can be considered as an effective method for the synthesis of carbonyl diazide.



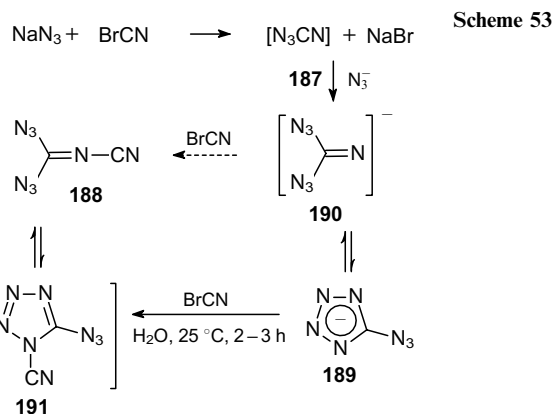
An advantage of $\text{FC}(\text{O})\text{Cl}$ as the starting material compared to $\text{C}(\text{O})\text{Cl}_2$ or $\text{C}(\text{O})\text{F}_2$ is that a stable intermediate product $\text{FC}(\text{O})\text{N}_3$ is generated in the first step *via* the rapid chlorine–azido substitution reaction. In the second step, this monoazide undergoes a slower fluorine–azide substitution reaction to afford $\text{OC}(\text{N}_3)_2$. In the condensed phase, diazide **3** is rather shock-sensitive; however, it demonstrates high thermal stability, as it did not decompose either in the gas phase or in the liquid and solid states. The solid melts at $16\text{ }^{\circ}\text{C}$ and can be transferred from one vessel to another by vacuum sublimation. Although Nolan *et al.*¹²⁸ did not indicate the yield of product **3**, the very fact of the isolation of carbonyl diazide in an individual state is particularly noteworthy. During thermal and photochemical decomposition of compound **3**, intermediates **184–186** can be generated (Scheme 52).



2.4.2. Carbamoyl diazides

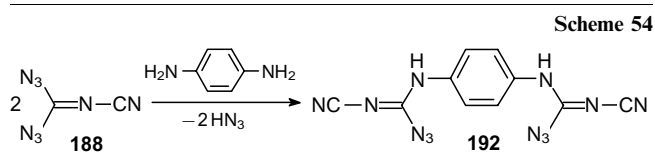
In 1912, Darzens and Hebd¹²⁹ carried out the reaction between bromocyan and sodium azide, assuming that they isolated cyanogen azide **187** as a product. Much later, it was revealed that the structure of the resulting compound was determined incorrectly and the reaction gave diazide **188** (Scheme 53), which is the first example of geminal diazide containing two azide groups on the unsaturated carbon atom.^{130–132}

The initial fast reaction of sodium azide with cyanogen bromide generates unstable intermediate **187**, which rapidly reacts with aqueous sodium azide to give tetrazole **189** in 80% yield. This tetrazole is believed to be formed through the attack of the azide ion on the electron-deficient carbon



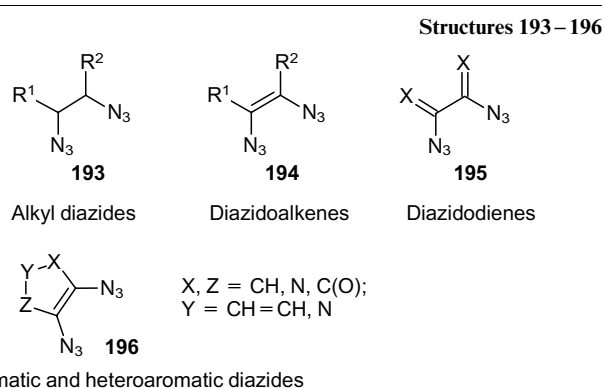
atom in intermediate **187**, which affords hypothetical geminal diazide **190**. The second, slower step involves the substitution yielding compound **191**, which apparently undergo ring opening to give *gem*-diazide **188**, which is typical of many tetrazoles.

Norris and Henry¹³³ reported the possible reaction of cyano-containing diazide **188** with *p*-phenylenediamine (Scheme 54); however, the authors did not provide the yield of product **192**.



3. Synthesis and transformations of vicinal diazides

Vicinal diazides comprise azido moieties located at the neighboring carbon atoms (Structures **193–196**). Derivatives of this class are commonly found in the literature as intermediates. In particular, they are precursors to vicinal diamines, the structural unit of which are found in many natural compounds and drugs,¹³⁴ and also play an important role in modern organic chemistry as ligands for catalysts for asymmetric synthesis.¹³⁵



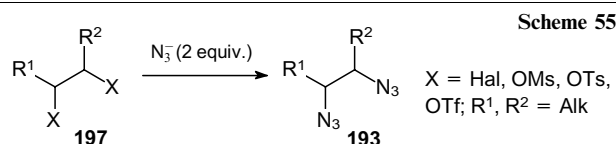
3.1. Methods for the synthesis of vicinal alkyl diazides

This Section considers the main methods for the preparation of aliphatic 1,2-diazides. The analysis of the literature data showed that the main approaches to the synthesis of such compounds include the nucleophilic substitution in dihalo, dihydroxy and sulfo derivatives of organic com-

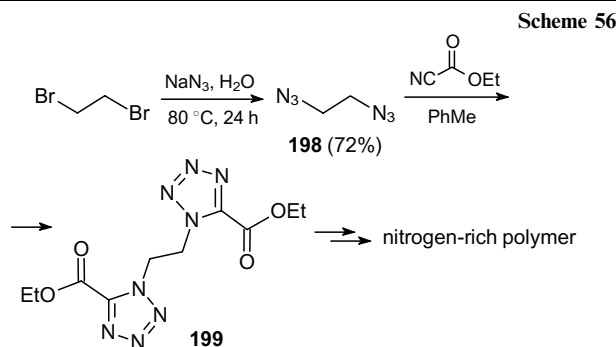
pounds, and also diazotization and diazo transfer reactions. Besides, vicinal alkyl diazides are derived from appropriate olefins.

3.1.1. Nucleophilic substitution reactions

The direct nucleophilic substitution of functional groups in derivatives **197** with an azide anion is the simplest and most reliable method for the synthesis of diazides **193** (Scheme 55).

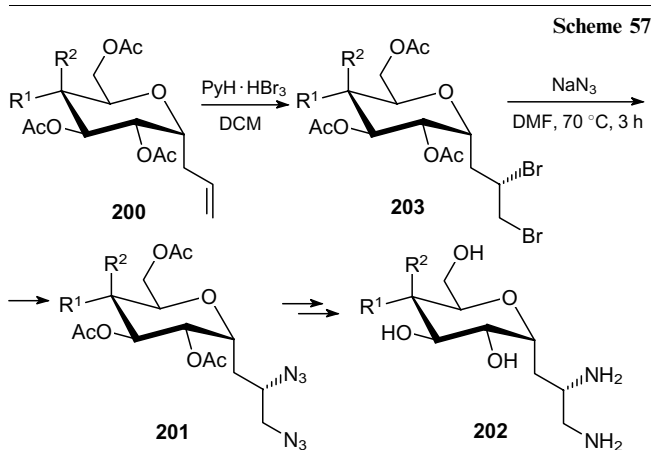


For example, 1,2-diazidoethane **198** can be obtained from dibromoethane *via* nucleophilic substitution under the action of sodium azide and then employed in the synthesis of thermally stable 1,2-bis(5-carboxyethyl-1*H*-tetrazolyl)ethane **199** (Scheme 56), a building block for the design of nitrogen-rich polymers.¹³⁶



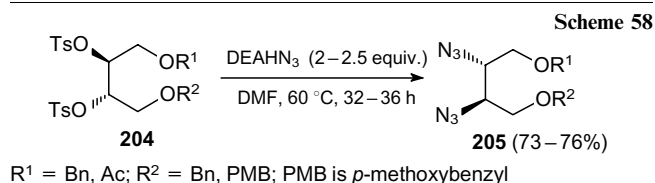
A number of publications^{137–141} describe the use of alkenes **200** in the preparation of vicinal diazides **201**, which served as substrates in the synthesis of diamines **202** (Scheme 57). In this case, the diazotization of dibromides **203** is carried out using NaN₃ to form the products in almost quantitative yields.

However, the reactivity of such alkali metal azides as NaN₃ and LiN₃ may be insufficient for the nucleophilic

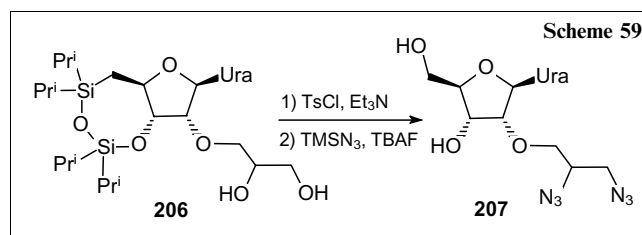


201: R¹ = OAc, R² = H (94%); R¹ = H, R² = OH (95%)

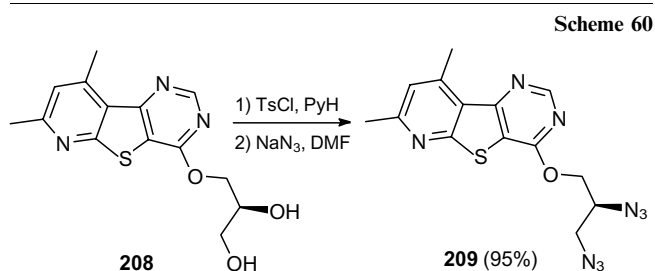
substitution of sterically hindered alkyl and alkenyl sulfonates. In this case, more reactive azide sources are generally employed, in particular, the reagent [Et₂NH₂]⁺N₃⁻ (DEAHN₃), which can be prepared by mixing an ethereal solution of HN₃ with diethylamine (DEA).⁶⁷ Thus, DEAHN₃ was successfully applied in the synthesis of diazides **205** from tosylates **204** (Scheme 58), and according to NMR spectroscopic data, the reaction occurred with almost complete inversion of both stereogenic centres.¹⁴²



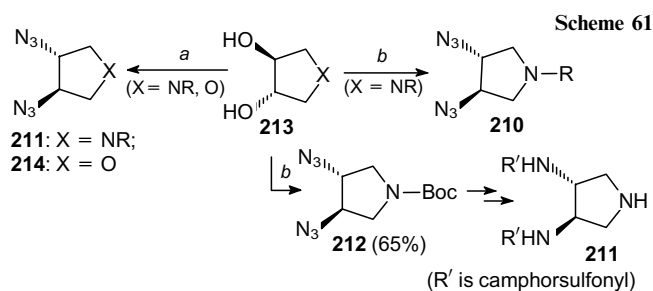
Another azidating agent, trimethylsilyl azide, proved effective in the nucleophilic substitution of OH moieties in uridine derivative **206** (Scheme 59).¹⁴³ Here, the azidation occurs in the presence of tetra-*n*-butylammonium fluoride (TBAF), which makes it possible to remove the silyl protection and obtain vicinal diazide **207**.



The azidation of diol **208** can also be accomplished in a two-step fashion to provide a high yield of the product (Scheme 60). First, the tosylation is carried out followed by the nucleophilic substitution with two equivalents of NaN₃ in DMF. This process makes available acyclic nucleoside analogues of pyridothienopyrimidines **209** containing a vicinal diazide moiety.^{144–147}



A similar strategy was used to prepare 3,4-diamino-1-substituted pyrrolidines.¹⁴⁸ Thus, Marson and Melling¹⁴⁹ synthesized diazides **210** in yields up to 63%, using LiN₃ as the azidating agent (Scheme 61). This approach has proven to be suitable for the synthesis of sulfonamides **211**, serving as promoters in the asymmetric addition of ZnEt₂ to *p*-chloroacetophenone, *via* the formation of diazide **212**.^{150–153} Reported also are successful attempts to carry out the Mitsunobu reaction^{154–156} for enantiomeric diols **213**, which were transformed into diazides **211** and **214**, when treated sequentially with HN₃, PPh₃ and diethyl azodicarboxylate (DEAD), in yields up to 80%.¹⁵⁷

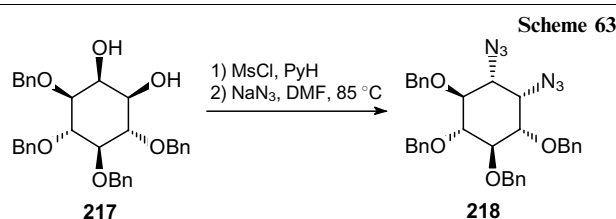


(a) HN_3 , DEAD, PPh_3 , PhH; (b) 1) MsCl, Et_3N ; 2) LiN_3 , DMF;
210: R = $n\text{-C}_8\text{H}_{17}$ (63%), cyclo- C_6H_{11} (42%), Ph (31%),
 $4\text{-IC}_6\text{H}_4$ (45%), 1,1'-biphenyl-2-yl (45%), $n\text{-C}_8\text{H}_{15}\text{O}$ (55%);
 Boc is *tert*-butoxycarbonyl

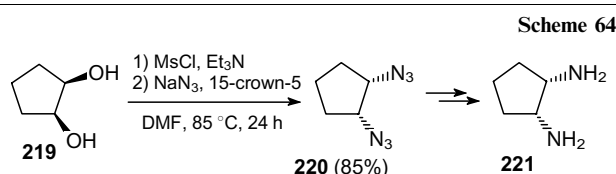
A simple and effective approach to 2,3-diaminocondur-
 itols, promising compounds with high biological activ-
 ity,^{158, 159} comprises the azidation of 4,5-dimesyl-3,6-
 dimethoxythiepane **215** with sodium azide in DMSO. This
 led to an inversion of configuration at the C(4) and C(5)
 atoms when forming diazide **216** (Scheme 62).^{160, 161}



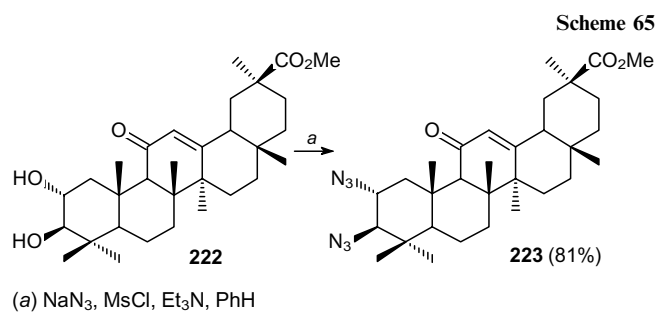
The two-step azidation of 3,4,5,6-tetra-*O*-benzyl-my-
 oinositol (**217**) was carried out under similar conditions in a
 DMF medium (Scheme 63). The yield of diazide **218** over
 two steps ranges from 54 to 79% according to various
 sources.^{162–164}



The mesylation of diol **219** followed by the treatment
 with NaN_3 in the presence of catalytic amounts of
 15-crown-5 provides diazide **220** in high yield (Scheme 64).
 This diazide **220** can be further reduced to diamine **221**,
 which is a precursor to chelating agents based on polyami-
 nocarboxylic acids.^{165, 166}

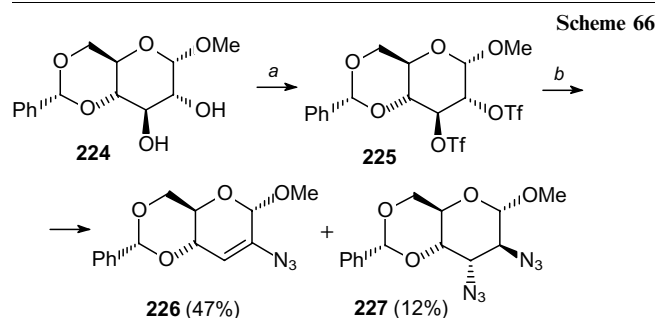


This approach has proven effective also for the synthesis
 of diazide-substituted terpenoids, *e.g.*, from diol **222**
 (Scheme 65).¹⁶⁷ Unfortunately, the authors failed to

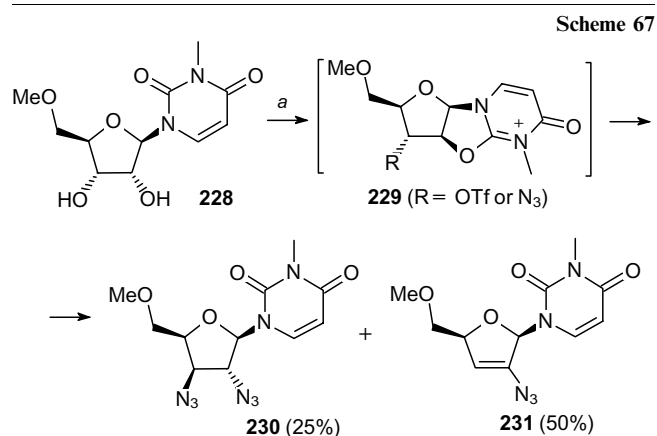


adequately justify the retention of stereoconfiguration of
 asymmetric centres in the synthesis of diazide **223**.

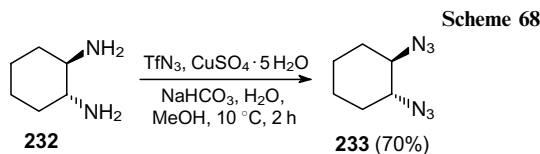
When ditriflates are used in the azidation, the resulting
 products can contain two good leaving groups and serve as
 valuable substrates for subsequent transformations.¹⁶⁸ At
 room temperature, triflate **225**, derived from protected
 glucoside **224**, reacts with tetra-*n*-butylammonium azide in
 THF to give a mixture of mono- (**226**) and diazidation (**227**)
 products (Scheme 66).



In a similar way, using trifluoromethanesulfonic anhy-
 dride, 2',3'-diamino-substituted uridines with *xylo* confi-
 guration can be produced from compound **228** (Scheme 67).¹⁶⁹
 In this case, the nucleophilic attack of an azide anion on the
 resonance-stabilized cation **229** occurs. As a result, two main
 products, diazide **230** and monoazide **231**, are obtained.
 Evidently, the latter product is generated *via* the
 elimination of HN_3 from diazide **230**.



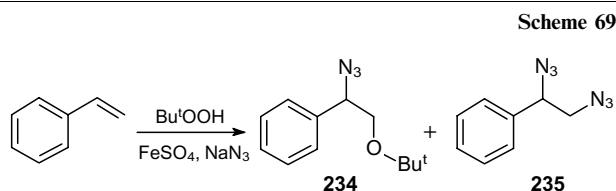
The diazo transfer reaction of 1,2-diaminocyclohexane (**232**) with triflyl azide afforded 1,2-diazidocyclohexane (**233**) in good yield (Scheme 68).¹⁷⁰



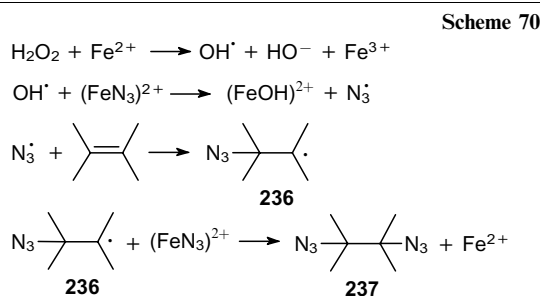
3.1.2. Synthesis of alkyl-1,2-diazides from alkenes

3.1.2.1. Stoichiometric 1,2-diazidation of olefins

The synthesis of vicinal diazides was first described in 1962.¹⁷¹ The iron(II)-catalyzed decomposition of *tert*-butyl hydroperoxide in the presence of styrene and NaN_3 produces a mixture of azidoether **234** and diazide **235** (Scheme 69). The authors provided no information on the ratio and yields of the products.

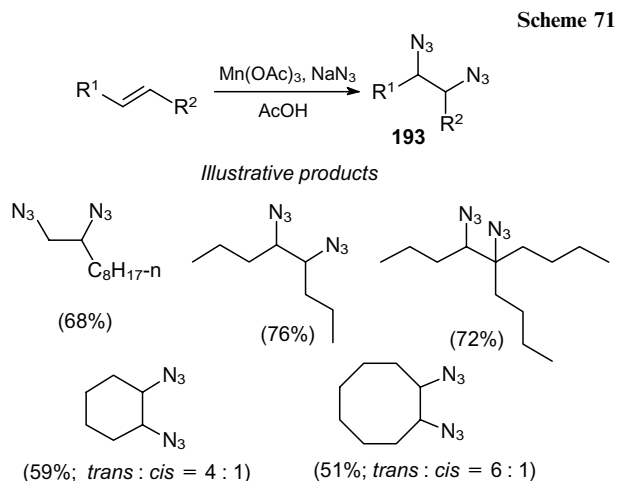


The mechanism of this reaction⁹⁹ involves a stepwise radical diazidation, as exemplified by 2,3-dimethylbut-2-ene in Scheme 70, which leads to the generation of azidoalkyl radicals **236** and the formation of vicinal diazide **237**.

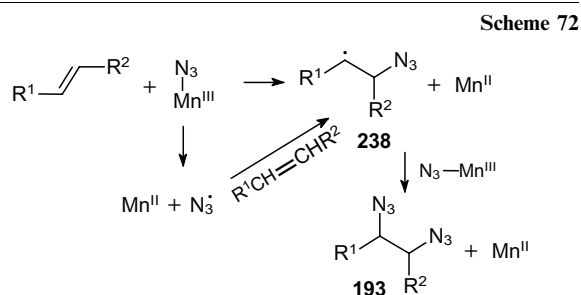


The pathway of the reaction between styrene and NaN_3 is driven by the electrophilic character of the reactive oxygen radical.¹⁷² Due to its high electrophilicity, the OH^\cdot radical reacts with the azide ion coordinated to the iron salt rather than with the olefin. The electrophilic character of the newly formed azide radical N_3^\cdot is not quite as pronounced as in the OH^\cdot radical. This reaction can be extended to conjugated dienes (butadiene, cyclopentadiene, *etc.*) and also applied to non-activated alkenes, such as pent-2-ene, hex-1-en, cyclohexene, *etc.* In the presence of electron-withdrawing groups attached to the double bond, such as in the case of acrylonitrile, the reaction proceeds less efficiently. There are examples of using lead¹⁷³ and thallium¹⁰⁰ salts as catalysts for such processes; however the yields of diazides turned out to be low.

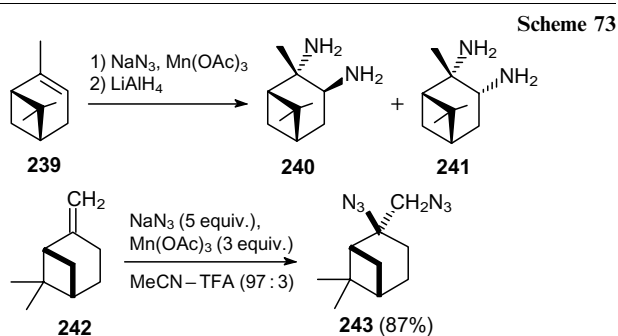
Alkenes can be converted into vicinal diazides **193** in moderate yields using an excess of NaN_3 in the presence of $\text{Mn}(\text{OAc})_3$ (Scheme 71).¹⁷⁴



The mechanism of this reaction involves the generation of azidoalkyl radical **238**, which reacts with the $\text{Mn}^{\text{III}}-\text{N}_3$ complex to afford vicinal diazide **193** (Scheme 72).

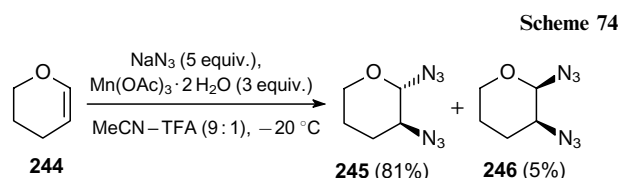


This approach was extended to the natural alkene α -pinene (**239**),¹⁷⁵ which gave a mixture of isomeric diamines **240** and **241** (Scheme 73). Meanwhile, β -pinene (**242**) can be regioselectively converted into the corresponding 1,2-diazide **243** in high yield.¹⁷⁶ The above procedure was modified and applied to other, more acid-sensitive alkenes.



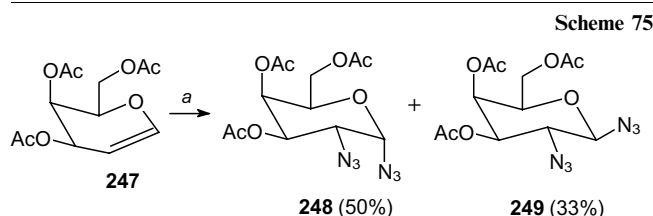
TFA is trifluoroacetic acid

Model experiments with dihydropyran **244** (Scheme 74) demonstrated that the diazidation in a $\text{Mn}(\text{OAc})_3-\text{NaN}_3-\text{AcOH}$ system proceeds much slower than the protonation of the double bond. Therefore, the reaction gives tetrahydropyranol and tetrahydropyranyl azide as the major products. Carrying out this reaction at a low temper-



ature in a 9:1 MeCN–TFA mixture significantly reduces the potential for protonation, thereby producing a mixture of *trans*- (**245**) and *cis*-diazides (**246**).

The same solvent system proved to be suitable for 1,2-diazidation using peracetylated or perbenzylated glycols as substrates. Thus, the reaction of 3,4,6-tri-*O*-acetyl-D-galactal (**247**) with a mixture of Mn(OAc)₃·2H₂O and NaN₃ with the same ratio, in a 9:1 MeCN–TFA mixture at 25 °C for 2 h affords a mixture of diazides **248** and **249** (Scheme 75). Such 2-azido-2-deoxyglycopyranosyl azides can be used to produce glycosylated asparagines.^{177, 178} The above examples sufficiently demonstrate the scope of the addition reaction of azide with alkenes in the presence of Mn(OAc)₃.

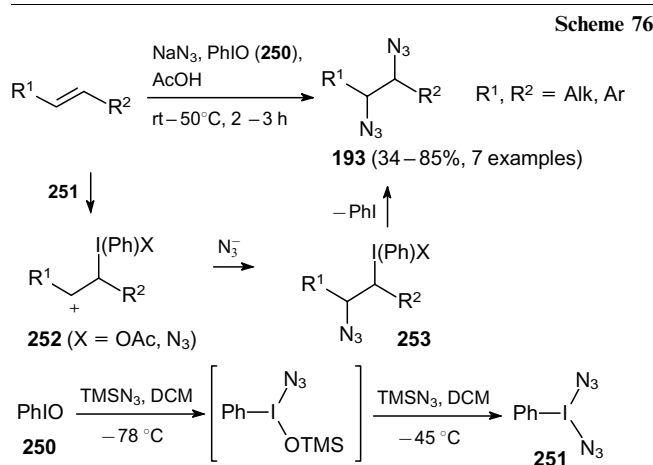


(a) NaN₃ (5 equiv.), Mn(OAc)₃·2H₂O (3 equiv.), MeCN–TFA (9:1)

3.1.2.2. 1,2-Diazidation using hypervalent iodine

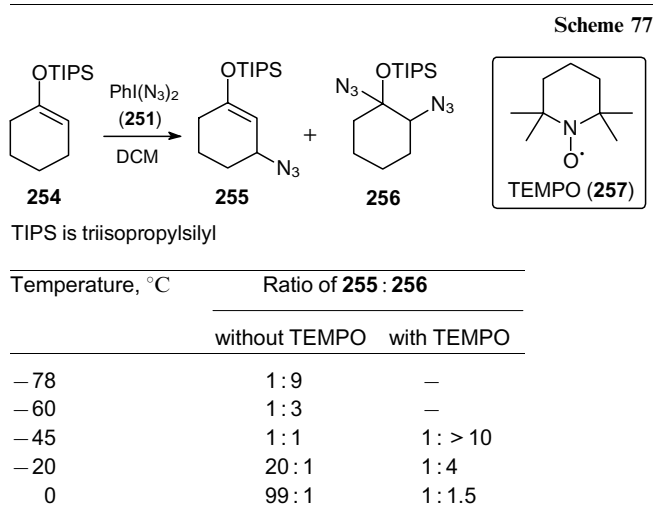
In recent years, reagents based on hypervalent iodine have gained great popularity in synthetic organic chemistry due to their low toxicity, ease of handling and commercial availability. Thus, an interesting approach to vicinal diazides is based on the reaction of alkenes with iodobenzene (**250**) in the presence of sodium azide (Scheme 76). This method provides a simple and efficient route to 1,2-diazides **193**, which can be prepared in yields up to 85%. Terminal alkenes and also disubstituted and cyclic olefins can be used in this process.¹⁷⁹

The reaction mechanism involves the electrophilic attack of the *in situ* formed diazide derivative of hypervalent

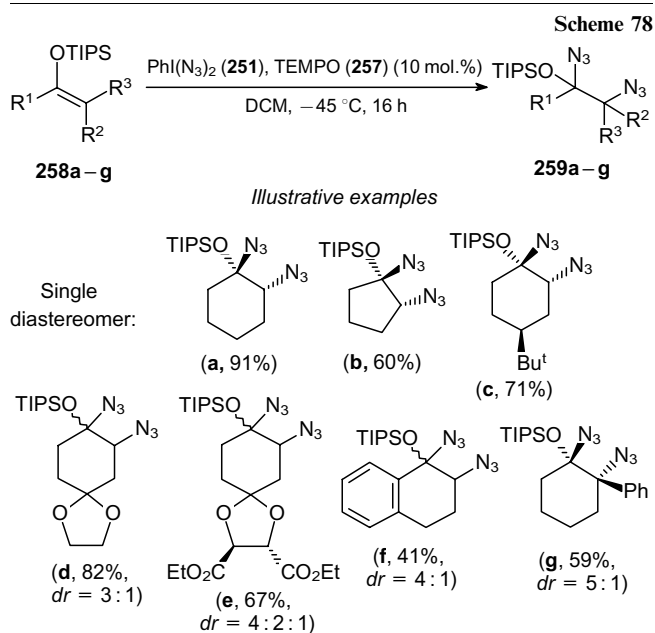


iodine **251** on the alkene double bond. This generates carbocation **252**, to which an azide anion then adds yielding intermediate **253**. The subsequent reductive elimination of iodobenzene affords vicinal diazide **193**. Alternatively, this step can be considered as the nucleophilic substitution of iodobenzene with an azide ion.

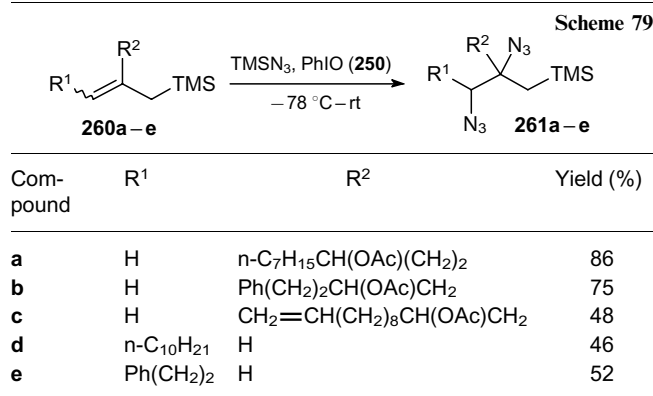
It was shown¹⁸⁰ that diazide **251** can act as an azidating agent for triisopropylsilylated enols **254**. Depending on the temperature conditions, the reaction can afford predominantly β-azide **255** or 1,2-diazide **256** (Scheme 77). Consequently, in this case there are two competing mechanisms; the authors suggested that the formation of diazide **256** occurs *via* the radical addition. The use of a stable organic radical (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO, **257**) allows the synthesis of diazidation product **256** as the major product.



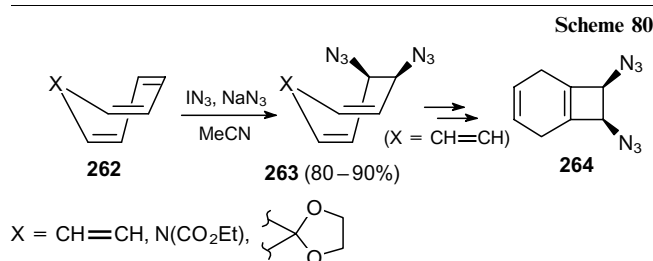
Under the optimized conditions, in the presence of TEMPO, TIPS-substituted enols **258a–g** gave rise to a large number of diazides **259a–g** in yields from 41 to 91%, with the products **259a–c** forming a single diastereomer (Scheme 78).



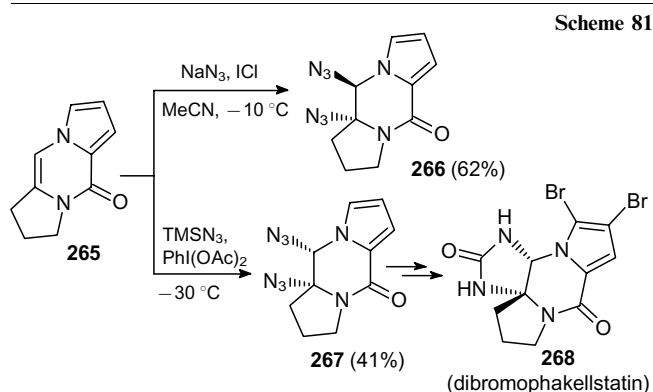
The reaction of β -substituted allylsilanes **260a–e** with iodosobenzene (1.5 equiv.) and TMSN_3 (2 equiv.) furnishes 1,2-diazides **261a–e** in yields up to 86% (Scheme 79).¹⁸¹



It is noteworthy that 1,2-diazides can be prepared by the reaction of cyclic conjugated polyolefins with IN_3 and an excess of NaN_3 affording the corresponding *cis* isomers.¹⁸² Thus, the reaction of cyclooctatetraenes **262** with iodine azide, prepared *in situ* from an excess of sodium azide and iodine monochloride in acetonitrile, gives a *cis* product of the general formula **263** (Scheme 80), however, for X = CH=CH, the diazide is rapidly transformed into bicyclic product **264**. Moreover, the reaction of cycloocta-1,3- and cycloocta-1,5-dienes under the above conditions produces monoazides, which can be further converted to the corresponding diazides when treated with NaN_3 in DMF at 35–40 °C.

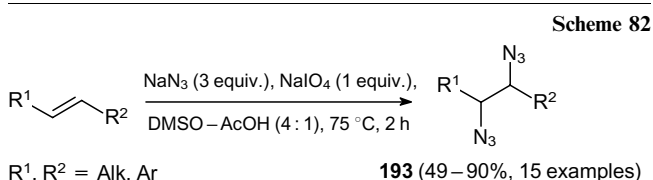


This approach was employed to azidate pyrazinone derivative **265** to form diazide **266** in moderate yield. When changing the reaction conditions, ketone **265** gave isomeric diazide **267**, which was used in the synthesis of the tetracyclic pyrrole imidazole alkaloid (\pm)-dibromophakell-**268** (Scheme 81).



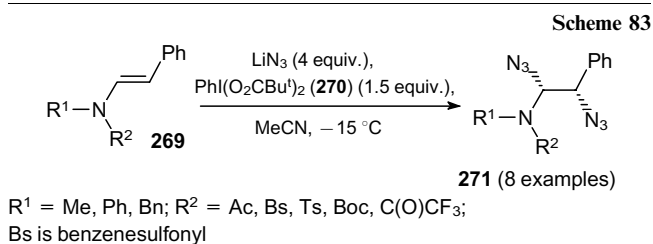
statin (**268**) isolated from the marine sponge *Agelas* (Scheme 81).¹⁸³

Another variant of the direct diazidation based on the use of the sodium periodate–sodium azide–DMSO–AcOH system is notable for its efficiency and simplicity.⁵² By varying the stoichiometric ratio of reactants, the optimal combination was identified, consisting of 3 equiv. of NaN_3 and 1 equiv. of NaIO_4 . Under these conditions, styrene derivatives and aliphatic olefins, including linear and cyclic alkenes, produce 1,2-diazides **193** in high yields (Scheme 82).



Internal olefins provide high yields of *syn*- and *anti*-isomeric products formed in a 1:1 ratio. However, no reaction occurs with α,β -unsaturated carbonyl compounds [e.g., cinnamic esters, (*R*)-(-)-carvone] and also sterically hindered alkenes (e.g., α -pinene). The process follows a radical pathway, since the diazidation of styrene in the presence of catalytic amounts of TEMPO resulted in a sharp decrease in the yield of the product (up to 10%) due to the radical quenching effect.

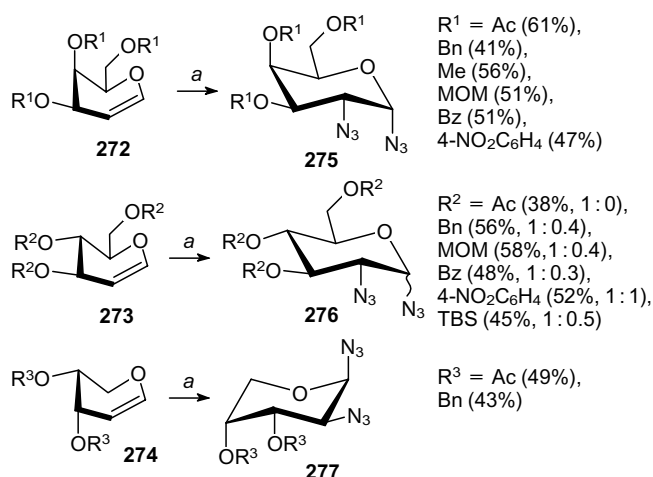
To diazidate double bonds, an approach can be employed based on the treatment of enamides **269** with a combination of bis(*tert*-butylcarboxy)iodobenzene (**270**) and LiN_3 in acetonitrile (Scheme 83).¹⁸⁴ The corresponding 1,2-diazides **271** are produced in yields ranging from 18 to 61%; high degrees of stereoselectivity of diazidation (up to 90% of *syn*-isomer) are achieved.



The diazidation of the double bond can also be performed using the bis(trifluoroacetoxy)iodobenzene (PIFA)– TMSN_3 system in the presence TMSOTf as a catalyst.¹⁸⁵ In particular, 1,2-unsaturated sugars **272–274** can be converted under these conditions to the corresponding vicinal diazides **275–277** in moderate yields (Scheme 84). While galactoses **272** produce the corresponding *cis*-1,2-diazide products **275**, glucoses **273** form mixtures of α - and β -anomers in different ratios (given in parentheses after the yield of the product), with α -anomer dominating. Interestingly, the reaction of arabinose derivatives **274** affords vicinal diazides **277** in the ¹C₄ conformation.

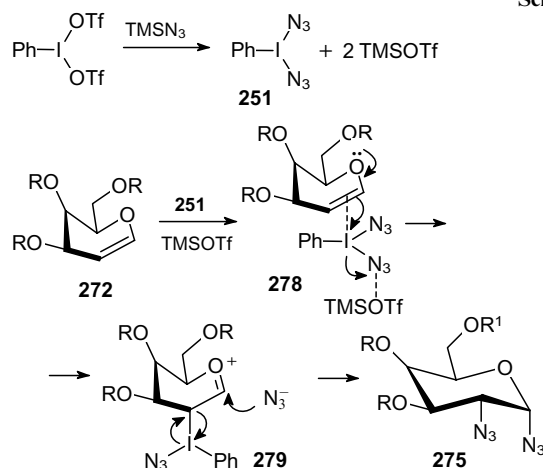
The mechanism of this reaction for derivatives **272** is illustrated in Scheme 85.¹⁸⁵ Diazide $\text{PhI}(\text{N}_3)_2$ (**251**) generated *in situ* produces intermediate **279** upon π -interaction (complex **278**) with the galactal double bond from the axial side. Then the azide moiety is transferred to the C(2) atom from the axial side in an S_{Ni} fashion. After this, due to steric

Scheme 84



(a) TMSN_3 (3 equiv.), PIFA (1 equiv.), TMSOTf (30 mol.%), DCM, -30°C ; MOM is methoxymethyl

Scheme 85



hindrance caused by the substituents at the C(3), C(4) and C(5) atoms, the second azide moiety preferentially attacks the anomeric carbon atom of the galactose derivative from the axial side to form diazide **275**.

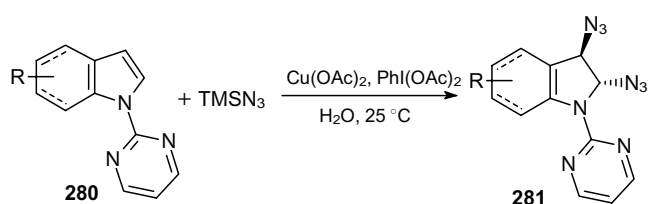
3.1.2.3. Catalytic 1,2-diazidation of olefins

Transition metal catalysts are also used to prepare vicinal diazides. Thus, the copper(II)-catalyzed 2,3-diazidation of indoles of the general formula **280**, involving azidotrimethylsilane as the azide source and iodobenzene acetate as the oxidant, provides a route to a series of 2,3-diazido-substituted indoles **281** in high yields (Scheme 86).¹⁸⁶

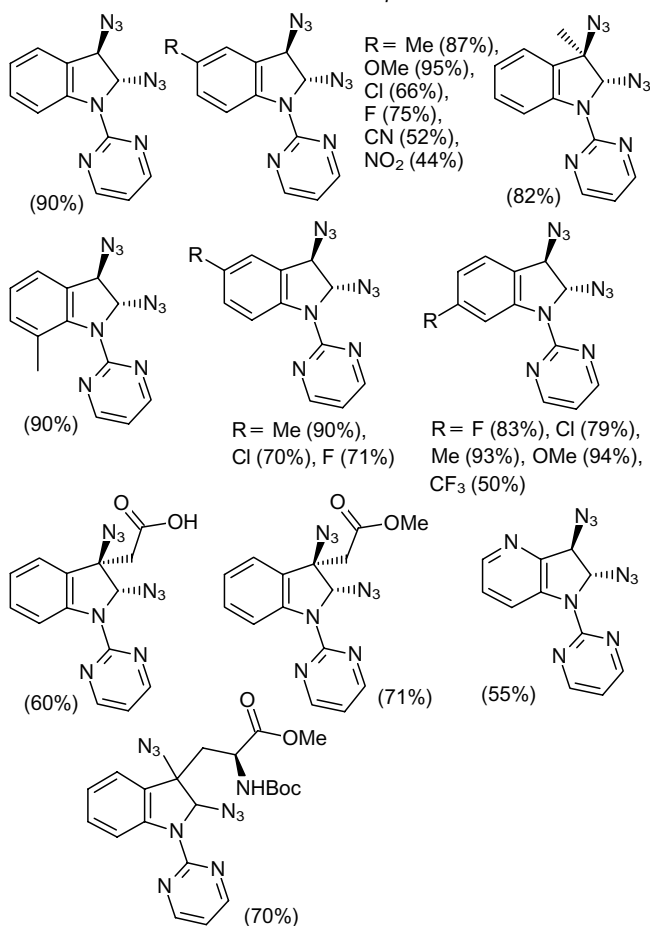
Indoles bearing electron-donating groups, such as Me and OMe, provide higher yields of the products compared to the substrates containing electron-withdrawing substituents. This reaction shows high diastereoselectivity and occurs under mild conditions in an aqueous medium.

The proposed mechanism involves the coordination of Cu(OAc)_2 by the pyrimidine ring of the substrate to afford complex **282** followed by the regioselective activation of the C–H bond at the C(2) position of indole, thereby yielding Cu^{II} complex **283**. Then the N_3 radical, that formed in the reaction of PhI(OAc)_2 with TMSN_3 , is coordinated to the Cu^{II} ion to form complex **284** (Scheme 87). After this, the N_3 group is rapidly inserted at the indole C(2) atom. This is

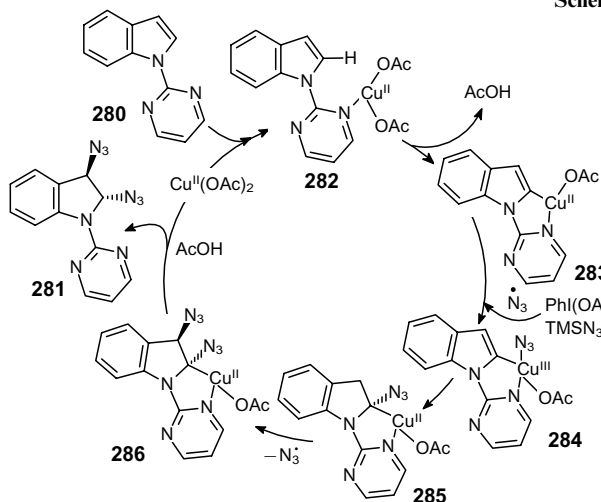
Scheme 86



Illustrative examples

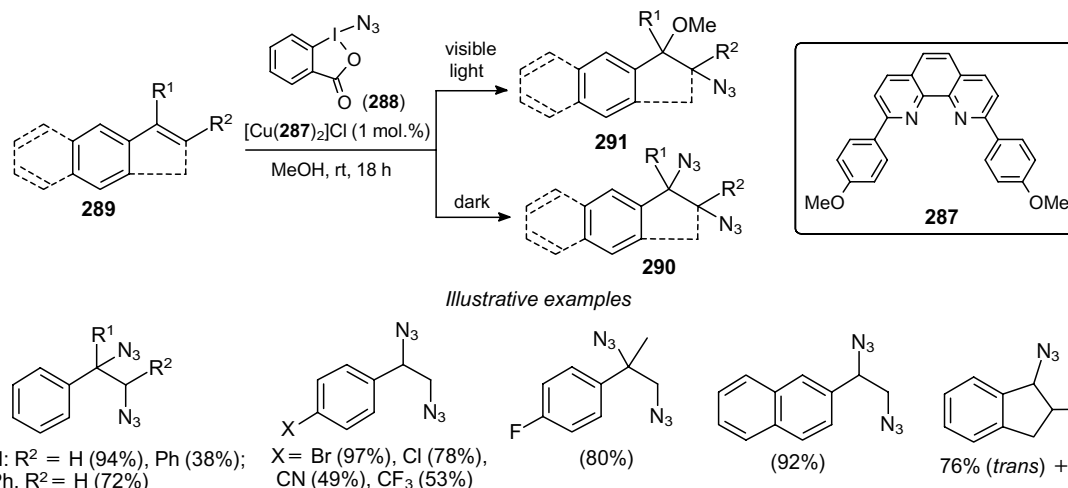


Scheme 87



accompanied by the dearomatization of the double bond at the C(2) and C(3) positions to give radical **285**. The

Scheme 88



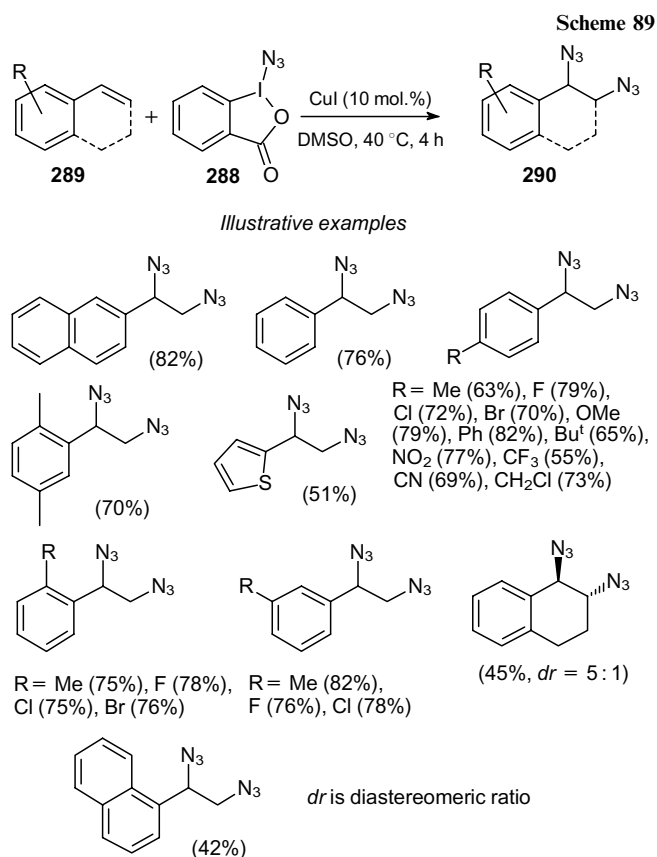
formation of *trans*-isomeric product **286** is due to the addition of the N_3 radical from the more accessible side of complex **285**.

Vicinal diazides **290** can be prepared by the addition of an azide group from Zhdankin reagent (1-azido-1,2-benzodioxol-3(1H)-one, **288**) to the double bond of various styrenes **289** using the catalyst $[\text{Cu}(\mathbf{287})_2]\text{Cl}$ (Scheme 88).¹⁸⁷ Under light irradiation, the azidation in a methanolic solution affords methoxyazides **291**. On the contrary, in the absence of light, double azidation takes place to furnish 1,2-diazides **290**. The reaction proceeds under mild conditions and performs well for a number of styrenes, 2-vinylnaphthalene and indene.

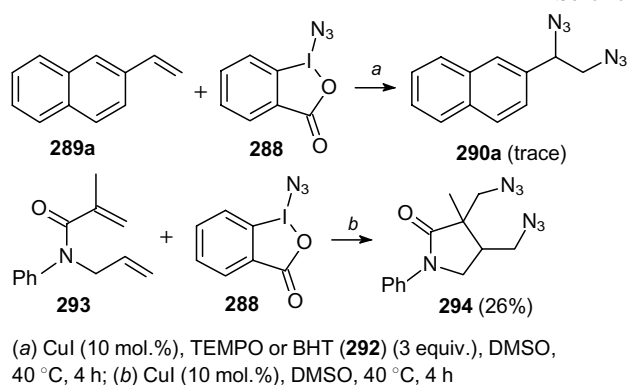
A similar procedure for the diazidation of styrenes **289** was developed by Lu *et al.*¹⁸⁸ They carried out the reaction in DMSO in the presence of catalytic amounts of $\text{Cu}(\text{OTf})_2$. By changing the catalyst to CuI , the authors increased the yield of the product up to 82%. Various *ortho*-substituted substrates react well under these conditions to afford diazidation products **290** in 75–78% yields. It should be noted that substrates bearing electron-withdrawing substituents give 1,2-diazides in good yields (55–77%). The reactions of 1-vinylnaphthalene and 2-vinylthiophene with Zhdankin reagent also produce the corresponding products in moderate yields. Finally, dihydronaphthalene gives a diazide in a fair yield with moderate diastereoselectivity (Scheme 89).

To investigate the mechanism of this transformation, the diazidation of 2-vinylnaphthalene (**289a**) was carried out in the presence of 3 equiv. of TEMPO or 2,6-di-*tert*-butyl-4-methylphenol (BHT, **292**) (Scheme 90 *b*). In both cases, a strong inhibition of the process was observed. Moreover, in the radical clock reaction, compound **293** gave cyclization product **294** in low yields. These observations suggest the radical mechanism of the process.

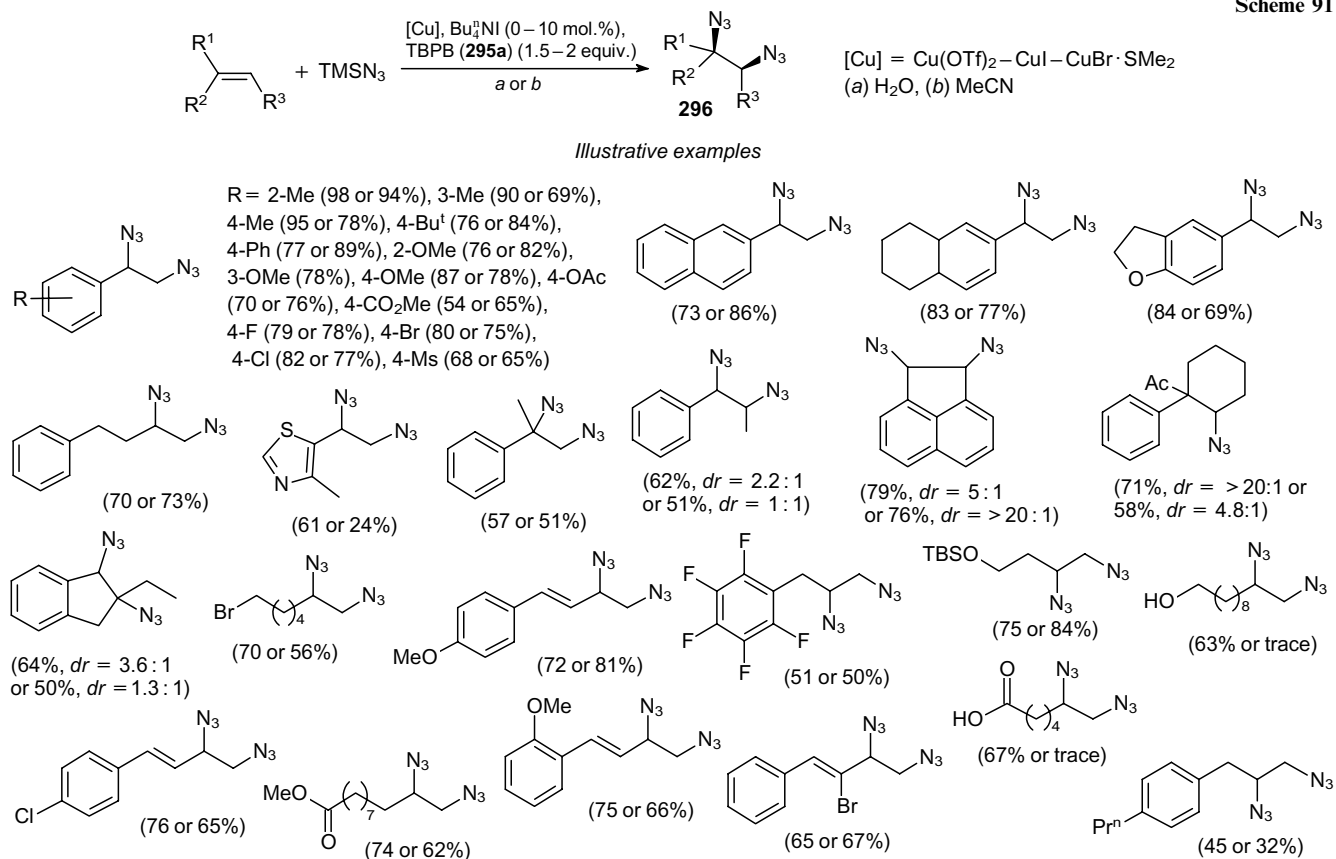
Zhou *et al.*¹⁸⁹ proposed the environmentally friendly copper-catalyzed ligand-free diazidation of olefins including vinyl(het)arenes, unactivated alkenes, as well as allenes and dienes, under mild conditions using TMSN_3 as the azide source (Scheme 91). This reaction occurs in the presence of *tert*-butyl peroxybenzoate (TBPB, **295a**) for 6 h and is implemented in two systems, namely, in water (method *a*, the yield is given in Scheme 91 as the first value in parentheses) and in MeCN (method *b*). Substrates bearing various substituents in aromatic rings produce the desired products **296** in yields up to 94%. Interestingly, the reaction



Scheme 90



Scheme 91



with cyclic olefins in various solvent systems affords diastereomers in different ratios. Diazides containing free hydroxy and carboxy functionalities are formed in trace amounts in an organic solvent; however, in water it is possible to obtain them in 63–67% yields. These reaction conditions are also suitable for dienes and allenes; under these conditions, the corresponding products were prepared in moderate yields.

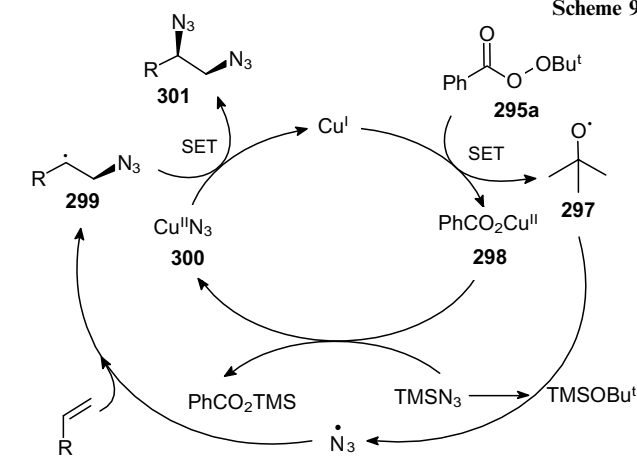
A radical catalytic cycle was proposed to explain the mechanism of this transformation. A single electron transfer (SET) between Cu^I and *tert*-butyl peroxybenzoate (**295a**) initiates the reaction of alkene RCH=CH₂ to generate the *tert*-butoxy radical (**297**) and Cu^{II} species (**298**). Then a radical relay process occurs between TMSN₃ and radical **297** yielding an azide radical, which adds to the starting olefin to give C-radical **299**. The ligand exchange produces intermediate Cu^{II}N₃ (**300**), which reacts with internal radical **299** to produce the desired diazidation products **301** and regenerate Cu^I (Scheme 92).

Iron(II) salts in the presence of pyridine-bis(oxazoline) ligand **302** are another type of catalysts for diazidation.^{190, 191} The use of trimethylsilyl azide–compound **303** catalytic system enables the diastereoselective diazidation of olefins at room temperature (Scheme 93).

This reaction provides a convenient route to vicinal primary diamines, as well as other synthetically valuable nitrogen-containing building blocks that are otherwise not readily available. To assess the scope of this diazidation method, a broad range of the starting olefins were tested. The target diazides **296** were obtained in yields up to 89%.

The mechanism of this type of diazidation (Scheme 94) involves the formation of azides **288** via the reaction of TMSN₃ with compound **303**. Azide **288** can be additionally

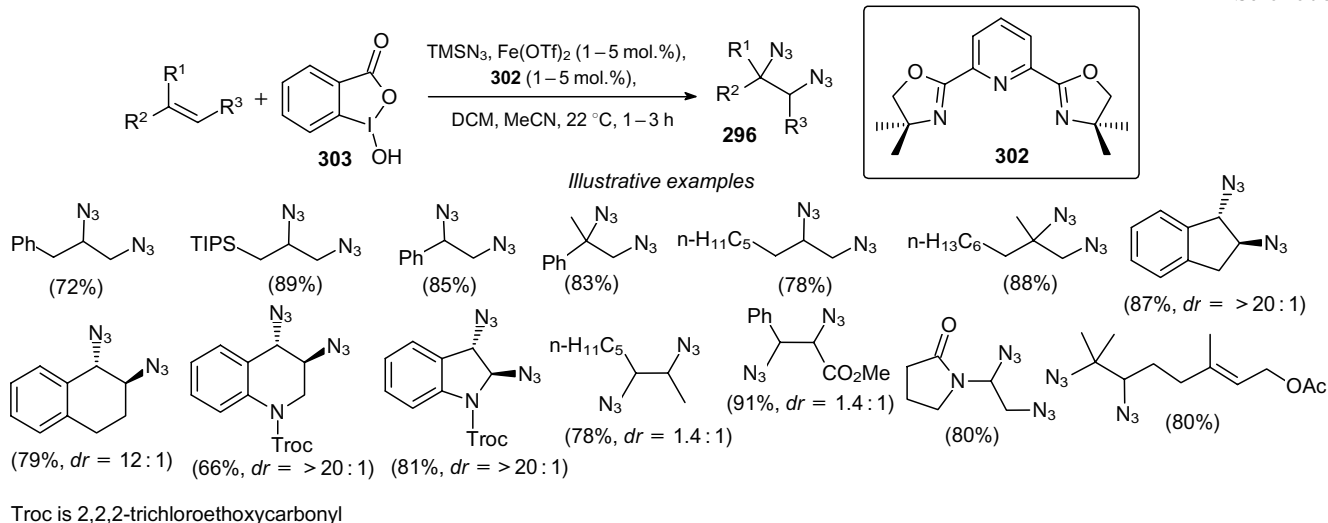
Scheme 92



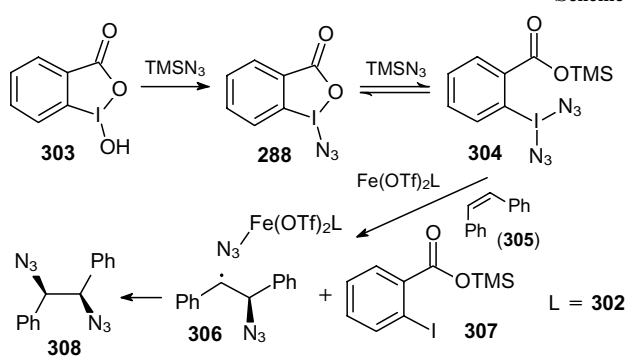
activated by trimethylsilyl azide to afford diazide **304**, which undergoes the I–N₃ bond cleavage in the presence of a Fe catalyst and presumably generates high-valent iron species and an azide radical. Thus, the azide radical can react, e.g., with *cis*-1,2-diphenylethylene (**305**) to form radical **306**, which is bound to the iron complex, and ester **307**. Finally, ferric species can further oxidize radical **306** through the azide transfer to the inner sphere of the complex to yield diazide **308**.

The reported iron-catalyzed direct diazidation¹⁹² is based on activation of stable peroxyesters **295** promoted by nitrogen-containing ligands (Scheme 95). In this case, nearly stoichiometric amounts of an oxidant and TMSN₃ are sufficient to carry out an efficient diazidation of a broad range of olefins and N-heterocycles at room temperature in

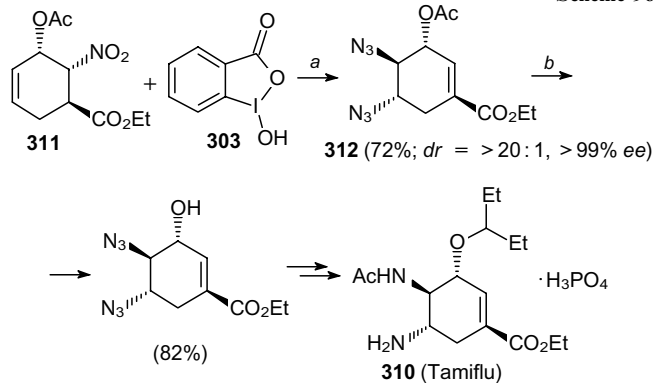
Scheme 93



Scheme 94

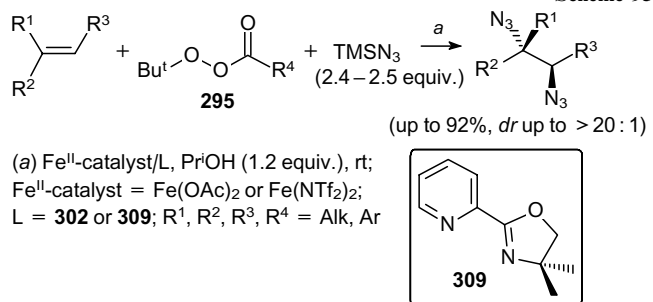


Scheme 96



(a) $\text{Fe}(\text{OAc})_2$ (5 mol.%), **302** (5 mol.%), TMSN_3 (5 equiv.), slow addition, DCM, MeCN, 22 °C; (b) MsOH, LiOH

Scheme 95



the presence of both tridentate (**302**) and bidentate (**309**) ligands. It is noteworthy that various substrates including allylic esters and carbamates, β -pinene, highly functionalized indoles, pyrroles (prone to rapid rearomatization), β,γ -unsaturated ketones enter this reaction to provide very high yields of the corresponding diazides.

Li *et al.*¹⁹³ carried out an enantioselective synthesis of the antiviral drug Tamiflu (**310**), in which the key *trans*-diamino moiety was formed *via* the iron(II)-catalyzed stereoselective diazidation of olefin **311** to give product **312** (Scheme 96). This method is efficient even for densely functionalized electronically deactivated substrates, for which the previously developed methods had limitations.

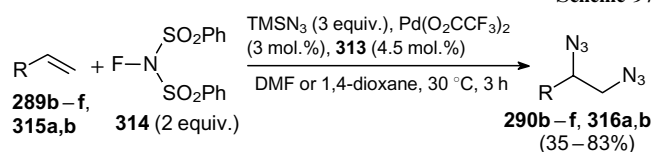
Other metals can also be used to deactivate alkenes. Thus, recently Peng *et al.*¹⁹⁴ reported the oxidative vicinal diazidation of unsaturated compounds catalyzed by

$\text{Pd}(\text{O}_2\text{CCF}_3)_2$ bearing the bidentate ligand [4,7-bis(4-bromophenyl)-1,10-phenanthroline (**313**)] in the presence of an azide source (TMSN_3) and an oxidant, *N*-fluorobenzene-sulfonimide (NFSI, **314**) (Scheme 97). Styrenes **289b–f** with various substituents at the *para* position proved to be suitable substrates to prepare the corresponding vicinal alkyl diazides **290b–f**. In the case of unactivated terminal alkenes **315a,b**, the addition of a small amount of *p*-nitrobenzoic acid and an increase in the amount of the catalyst to 5 mol.% are required, which improve the yields of products **316a,b** up to 83%.

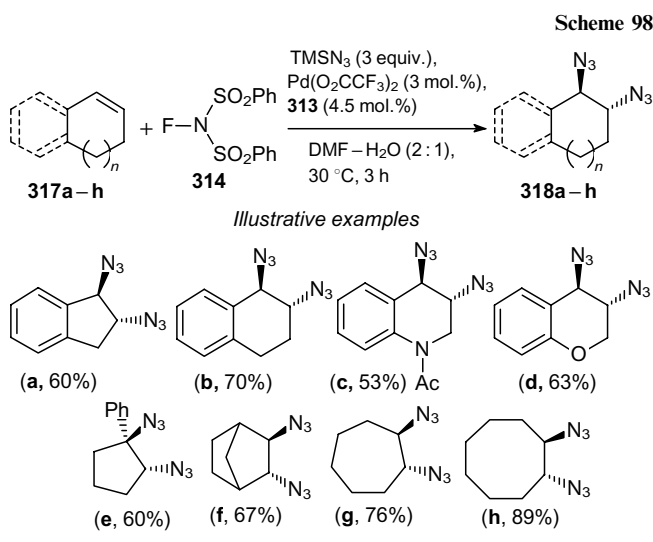
Using this approach, the corresponding *trans*-diazides **318a–h** can be obtained from cyclic alkenes **317a–h** (Scheme 98).

Originally, 1*H*-indene gave diazide **318a** in 70% yield with a 2:1 diastereomeric ratio under standard conditions.

Scheme 97

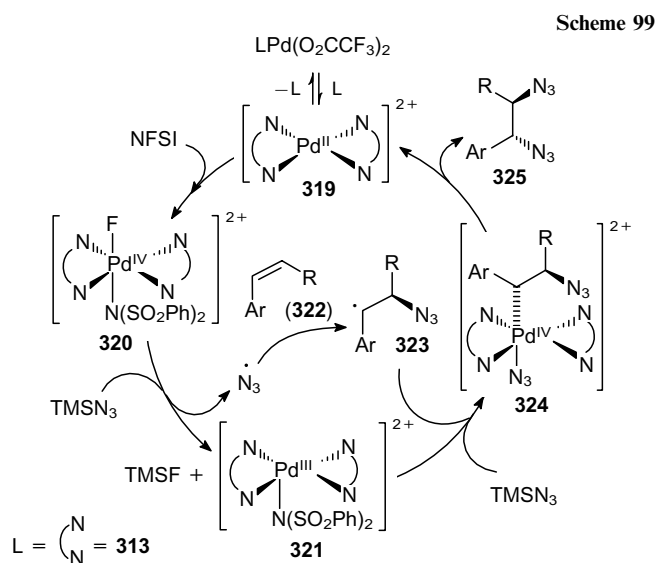


289, 290: R = 4- XC_6H_4 [X = H (**b**), Me (**c**), Bu^t (**d**), Br (**e**), Cl (**f**)]; **315, 316**: R = *n*- C_6H_{13} (**a**), CH_2Bn (**b**)



However, the diastereoselectivity was improved to $dr = 10:1$ by adding water as a cosolvent. A similar result was observed for 1,2-dihydronaphthalene **317b**. It should be noted that reactions of 1,2-dihydroquinoline and 2*H*-chromene afforded *trans*-isomeric products **318c,d** as single isomers in moderate yields. Interestingly, the reaction of α -phenylcyclopentene also showed an excellent diastereoselectivity, since it provides a single isomer **318e** in 60% yield. Unactivated cyclic alkenes containing five–eight-membered rings were found to give products **318f–h** in good yields with moderate diastereoselectivity $dr = (3–5):1$.

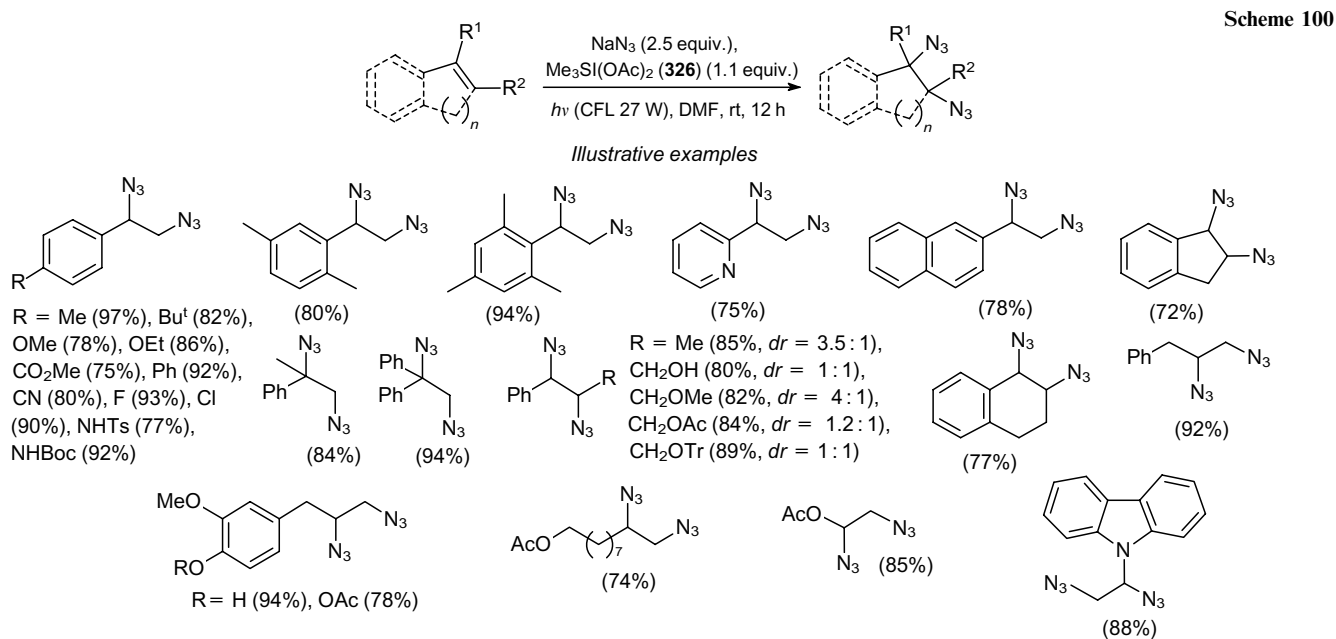
The mechanism of these transformations involves the oxidation of cationic complex **319** with *N*-fluorobenzene-sulfonamide (**314**) to give complex **320**. The latter oxidizes TMSN_3 via a single electron transfer to generate an azide radical and complex **321**. Then the azide radical adds to alkene **322** to yield C-radical **323**, which reacts with intermediate **321** to afford Pd^{IV} compound **324**. The subsequent ligand exchange and reductive elimination give rise to vicinal diazide **325** (Scheme 99).

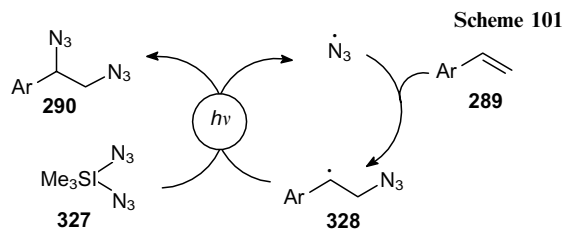


3.1.2.4. Photochemical 1,2-diazidation of olefins

The double azidation of alkenes can be carried out photochemically without the use of photoredox or metal catalysts.¹⁹⁵ The reaction proceeds stereospecifically under visible light irradiation and involves sulfonium bis(acetoxyl)iodate(I) ($\text{Me}_3\text{SI}(\text{OAc})_2$, **326**) and sodium azide as the radical source. Various vinylarenes and unactivated alkenes readily undergo 1,2-diazidation. It is important to note that sterically hindered 2,4,6-trimethylstyrene forms a diazide in high yield. Under these conditions, the diazidation of 2-vinylpyridine and 2-vinylnaphthalene was successfully carried out (75–78% yields). Indene and 1,2-dihydronaphthalene are converted into the corresponding vicinal *syn*-1,2-diazides in 72–77% yields with good diastereoselectivity ($dr = 96:4$) (Scheme 100).

The mechanism of this transformation involves the *in situ* formation of $\text{Me}_3\text{SI}(\text{N}_3)_2$ (**327**) and its subsequent visible light-induced homolysis. In this case, an electrophilic azidyl radical is generated, which attacks the $\text{C}=\text{C}$ bond, e.g., of alkene **289** to give benzylic radical **328**. Then the





azide radical derived from an iodonium salt adds to radical **328** to yield diazide **290** and a free azide radical, which can reattack the alkene molecule (Scheme 101).

3.1.2.5. Electrochemical 1,2-diazidation of olefins

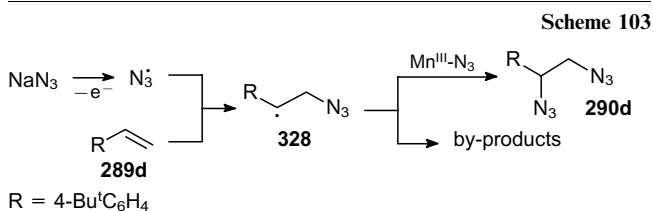
One of the electrochemical diazidation methods reported in the literature is a double azidation using a reticulated vitreous carbon anode in 0.1 M LiClO₄ solution in MeCN with an applied cell potential (E_{cell}) of 2.3 V. Manganese(II) bromide was used served as the catalyst; acetic acid, as the proton source.^{196, 197} This protocol is applicable to diazidation of a broad range of alkenes (Scheme 102). For example, aryl-substituted acyclic alkenes give the corresponding 1,2-diazides in 66–95% yields.

1,2-Diazides can be produced from terminal and also 1,1- and 1,2-disubstituted olefins under these conditions. Cyclic alkenes are also suitable substrates for this reaction, forming mainly *trans*-1,2-diazides in high yields with good diastereoselectivity. Electron-rich benzofuran and *N*-tosylindole were dearomatized to 1,2-diazides in yields of 78 and 69%, respectively. Substrates bearing hydroxy, carbonyl, carboxy, amine, sulfide or alkyne moieties, which react

without undesired side reactions, are suitable for this reaction system.

It is believed that the anodic generation of an azide radical followed by its addition to the double bond of, e.g., alkene **289d** and to intermediate radical adduct **328** results in the formation of two new C–N bonds and gives rise to vicinal diazide **290d** (Scheme 103). This catalytic system combines high reactivity and good chemoselectivity.¹⁹⁸

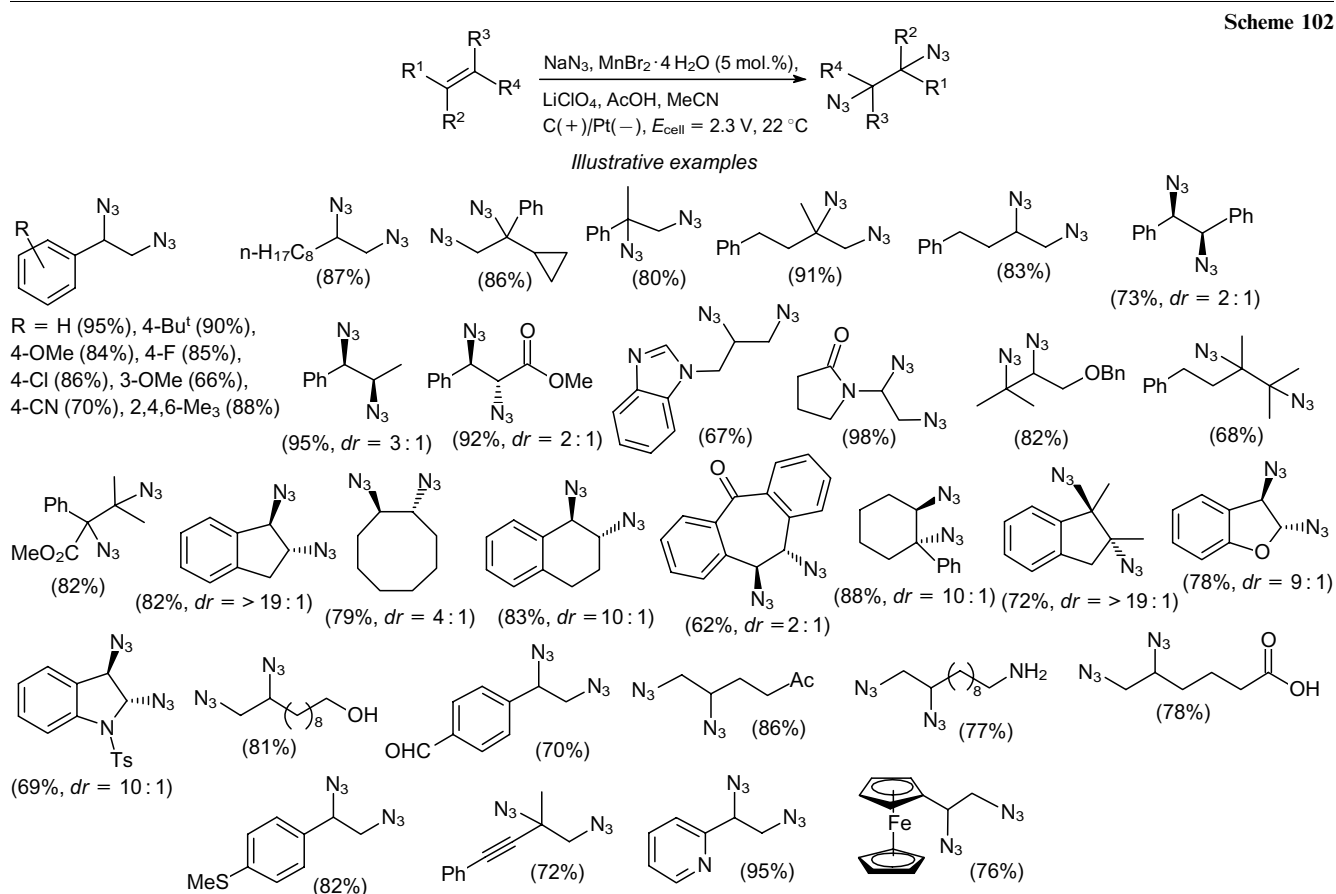
Recently, the aminoxyl catalyst CHAMPO (**329**) has been developed for the electrochemical diazidation of a wide range of alkenes to produce the corresponding diazides (Scheme 104).¹⁹⁹



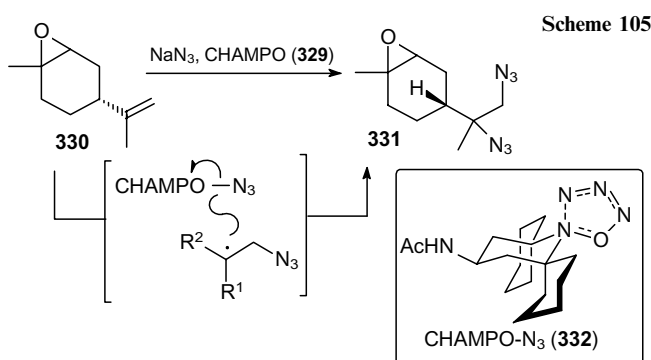
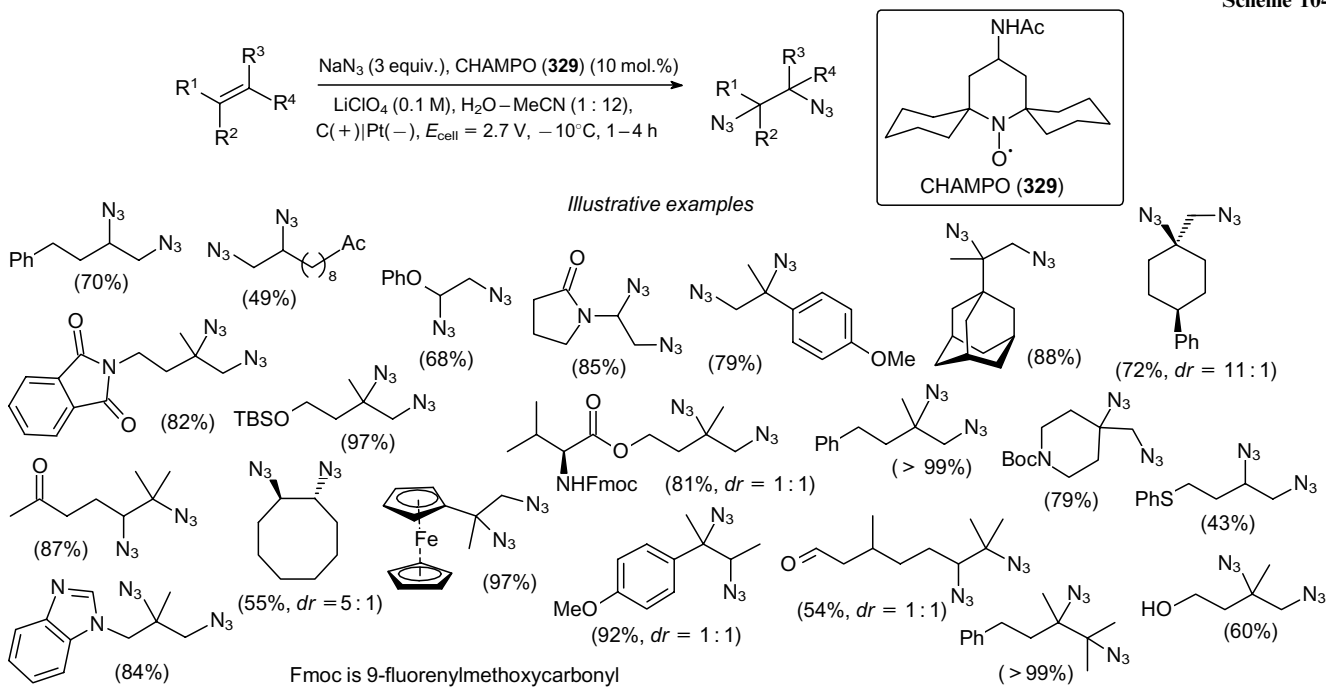
The radical diazidation of alkene **330** to product **331** by an anodically generated charge-transfer complex in the form of CHAMPO-N₃ (**332**) was achieved without using transition metal complexes or oxidants (Scheme 105).¹⁹⁹

3.2. Synthetic approaches to vicinal diazidoalkenes

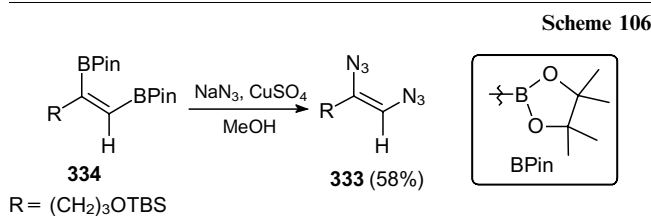
Literature data on the preparation of 1,2-diazidoalkenes are limited to only two examples including the substitution of 1,2-diboronic esters involving Cu^{II} species and the treatment of propargyl azides with an alternative azide source.



Scheme 104

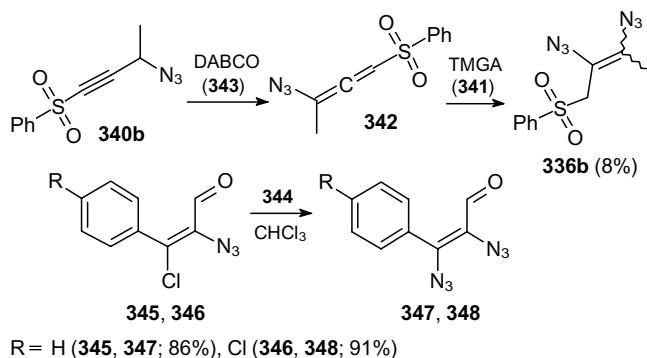
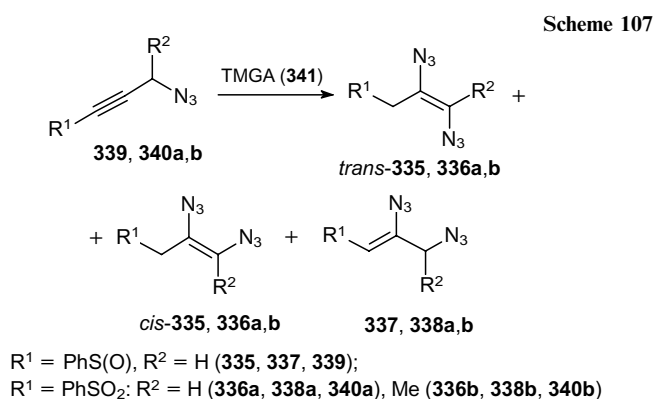


Mali *et al.*²⁰⁰ developed a versatile stereoselective route to the synthesis of (*Z*)-1,2-diazoalkenes **333** from the appropriate 1,2-diboronate esters **334** via the copper-mediated reaction with sodium azide (Scheme 106). This transformation occurs with the retention of stereochemistry of the original double bond. The mechanism of this transformation was not considered.



Open-chain 1,2-diazoalkenes **335**–**338** were obtained from propargyl azides **339**, **340**, bearing an acceptor substituent at the triple bond by the reaction with tetramethylguanidinium azide (TMGA, **341**) (Scheme 107).

In some cases, such products are prepared *via* a two-step procedure. The transformation sequence begins with the *in situ* formation of the corresponding azidoallene **342** in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO, **343**) followed by the addition of hydrazoic acid derived



from TMGA.²⁰¹ These diazides are extremely unstable; however, the introduction of electron-withdrawing substituents and the use of another N_3 source, tri-*n*-butylhexadecylphosphonium azide (**344**), allows the synthesis of *cis*-diazide products **347**, **348** from cinnamic aldehydes **345**, **346** in high yields.

3.3. Synthesis of aromatic and heteroaromatic vicinal diazides

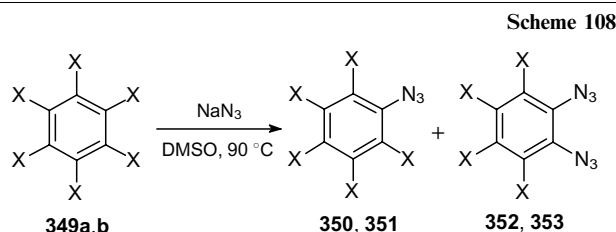
This Section considers approaches to the synthesis of aromatic and heteroaromatic (pyridinic, pyrrolic, *etc.*)

1,2-diazides *via* the nucleophilic substitution and diazo transfer reactions.

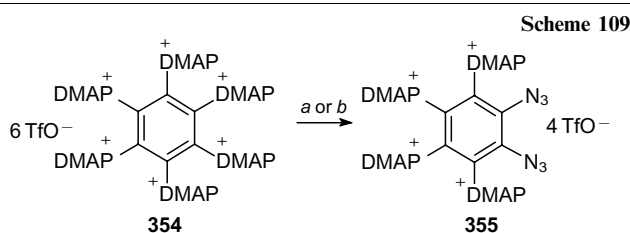
3.3.1. Synthesis of aromatic 1,2-diazides

3.3.1.1. Substitution reactions

Perchloro- and perbromobenzenes **349a,b** undergo selective dehalogenation when heated with an excess of sodium azide in dimethyl sulfoxide; the resulting mixture contains mainly monoazide (**350**, **351**) and 1,2-diazide (**352**, **353**) (Scheme 108).²⁰²



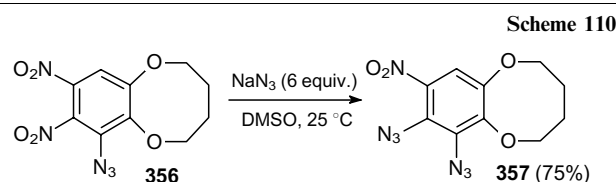
As part of the study on the reactivity of hexakis[4-(dimethyl)pyridinio]benzene hexakis(trifluoromethanesulfonate) (**354**) towards various nucleophiles, Weiss *et al.*²⁰³ treated a suspension of this compound in acetonitrile with azide ions and obtained salt **355** (Scheme 109).



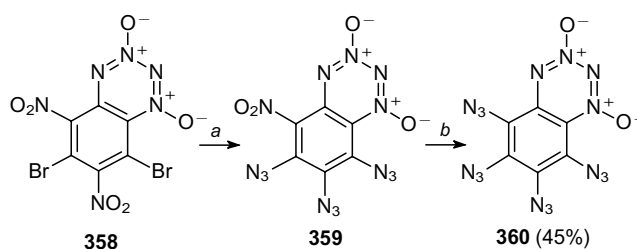
Sodium azide and TMGA (**341**) were used as azide sources. In the case of sodium azide, the amount of exchanged onio ligands can be affected by the presence of water, which reduces the nucleophilicity of the azide ions due to solvation. The use of TMGA as the azide source makes it possible to control the degree of onio exchange *via* stoichiometry. Reactions with NaN₃ often produces mixtures of mono- and diazides, as well as sodium triflate, which is difficult to remove from the reaction mixture. Therefore, TMGA is a more preferable azide source.

Treating of 7-azide-8,9-dinitro-2,3,4,5-tetrahydrobenzo[*b*][1,4]-dioxocin (**356**) with an excess of NaN₃ in DMSO results in the substitution of the nitro moiety to afford 7,8-diazide **357** in good yield (Scheme 110).²⁰⁴

The reaction of benzo-1,2,3,4-tetrazine 1,3-dioxide **358** with sodium azide in aqueous acetone gives triazide **359** (88% yield).²⁰⁵ Its subsequent treatment with NaN₃



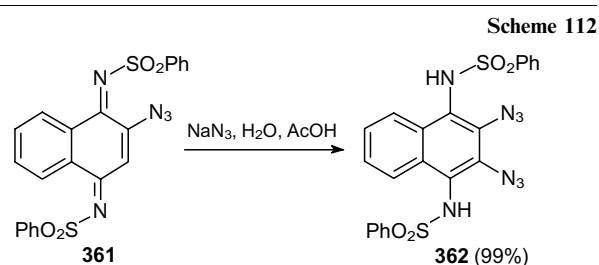
Scheme 111



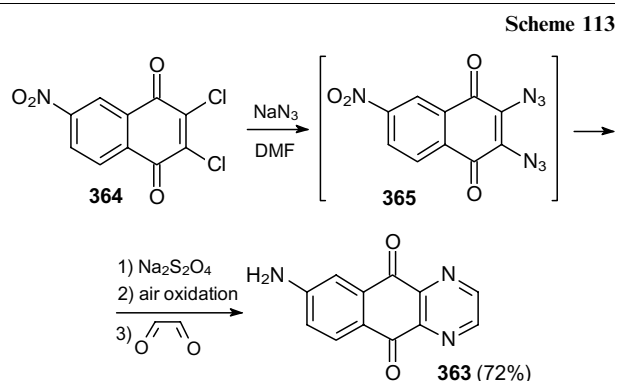
(a) NaN₃, H₂O, Me₂CO, 20 °C; (b) NaN₃, DMF, 20 °C

(1 equiv.) in DMF produces the corresponding tetraazide **360** (Scheme 111).

Adams and Moje²⁰⁶ used monoazide derivative **361** to prepare 2,3-diazido-1,4-naphthalenebenzenesulfonamide **362** in quantitative yield (Scheme 112).



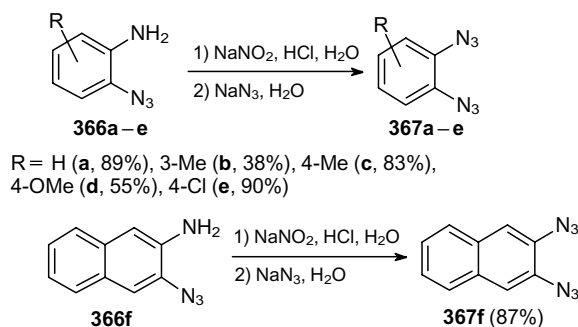
The synthesis of 6-amino-1,4-diazaanthraquinone **363** involves the nucleophilic substitution of dichloronaphthoquinone **364** to produce *in situ* 2,3-diazido-6-nitronaphthalene-1,4-dione (**365**) as an intermediate (Scheme 113).²⁰⁷ The resulting diazide is then reduced with sodium dithionite and oxidized with ambient oxygen to the corresponding diamino derivative, which reacts with glyoxal to afford diazaanthraquinone **363**. The formation of diazide **365** was confirmed experimentally.²⁰⁸ A number of studies^{209–220} reported similar examples of the nucleophilic substitution involving dihalobenzoquinone and -naphthoquinone derivatives to afford vicinal diazides.



3.3.1.2. Diazotization and diazo transfer reactions

The diazotization of 2-azidoanilines **366a–e** followed by the treatment of a diazonium salt solution with sodium azide forms the basis for the conventional synthesis of aromatic vicinal diazides, 1,2-diazidobenzenes **367a–e** (Scheme 114).^{221–223} In a similar way, 2,3-diazidonaphtha-

Scheme 114



lene **367f** can be prepared from aminoazide **366f** in high yield.²²⁴

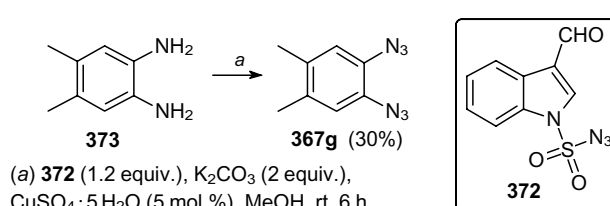
The double diazo transfer reaction was carried out to synthesize 1,2-diazobenzene **367a** from *o*-phenylenediamine **368** (Scheme 115).^{225,226} The mechanism of this transformation involves the deprotonation of the substrate giving dilithium derivative **369**, which is then converted to intermediate **370** following the addition of azidotris(diethylamino)phosphonium bromide. Subsequently, *via* the formation of zwitterion **371**, two tris(diethylamino)phosphorimine molecules are eliminated to give 1,2-diazide **367a** in 84% yield.

Mishra and Tiwari²²⁷ proposed another diazo-transfer reagent, namely, indole-3-carboxaldehyde-1-sulfonyl azide (**372**), which reacts with primary amines, including vicinal diamine **373**, in the presence of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and K_2CO_3 to yield diazide **367g** (Scheme 116).

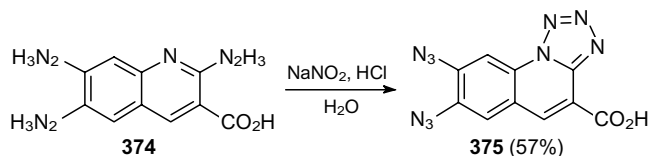
The treatment of 2,6,7-trihydrazinylquinoline-3-carboxylic acid (**374**) with nitrous acid affords tetrazoloquinoline **375** (Scheme 117).²²⁸

The effect of substituents at the positions 2 and 3 of quinoxaline 1,4-dioxides **376a,b** on the reactivity of fluorine atoms towards various nucleophiles, including NaN_3 , was studied.²²⁹ Quinoxaline 1,4-dioxide **376a**, when heated with an aqueous NaN_3 solution (1 : 1 molar ratio) in acetonitrile, gives a product of monosubstitution of fluorine in 63% yield, while using 2 equiv. of NaN_3 , diazido derivative **377a** is formed. However, the monosubstitution product was not isolated in the reaction of 2,3-dimethyl-substituted quinoxaline 1,4-dioxide **376b** with NaN_3 . These results indicate that an azido functionality facilitates the further substitution of the fluorine atom at the position 6 and, consequently, the second fluorine atom is substituted more rapidly than the first one (Scheme 118).

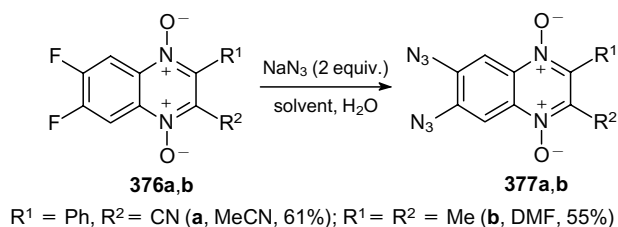
Scheme 116



Scheme 117



Scheme 118



3.3.2. Synthesis of heteroaromatic 1,2-diazides.

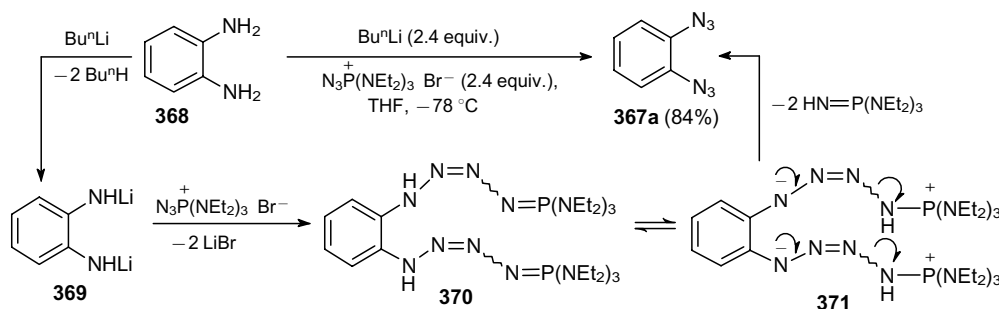
Substitution reactions

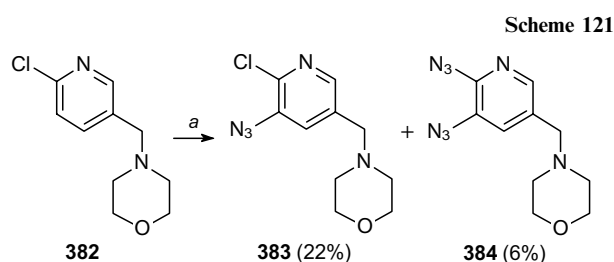
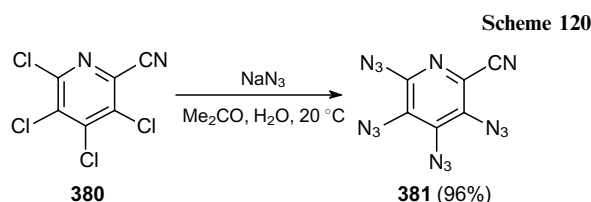
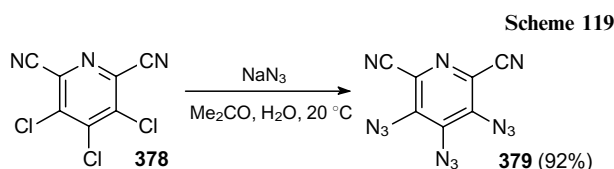
The reaction of trichloropyridine-2,6-dicarbonitrile **378** with an excess of azide in aqueous acetone at room temperature provides a high yield of triazidopyridine **379**, a promising component of energetic materials (Scheme 119).²³⁰

In 2009, the same research group²³¹ prepared tetraazido-substituted pyridine **381** from substrate **380** under identical conditions in almost quantitative yield (Scheme 120).

It is also possible to introduce an azide functionality into pyridine *via* metalation with the followed by the use of tosylamide as an electrophilic agent.²³² The starting chloro-substituted pyridine **382** was first lithiated with lithium diisopropylamide (LDA) and then TsN_3 was added to the reaction mixture. As a result, azidopyridine **383** and diazidopyridine **384**, as a by-product, were obtained (Scheme 121). Diazide **384** is unstable and decomposes within 16 h at room temperature.

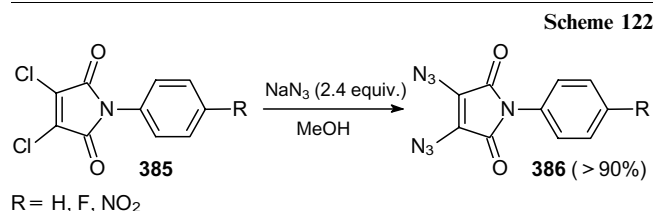
Scheme 115



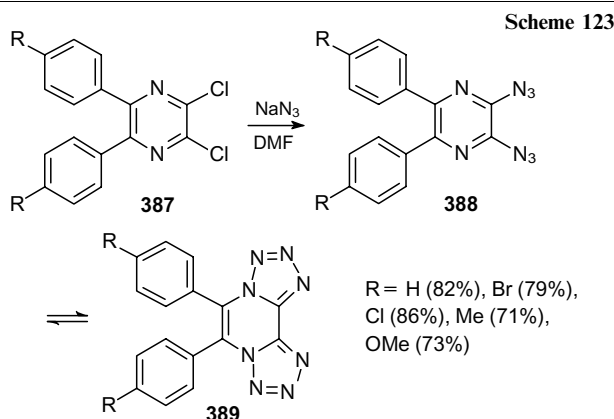


(a) 1) LDA, THF, hexane, -78°C ; 2) TsN_3 , THF, $-78-0^\circ\text{C}$

Under conventional diazidation conditions, *N*-aryldichloromaleimides **385** give *N*-arylmaleimidediazides **386** in high yields (Scheme 122).^{233, 234}



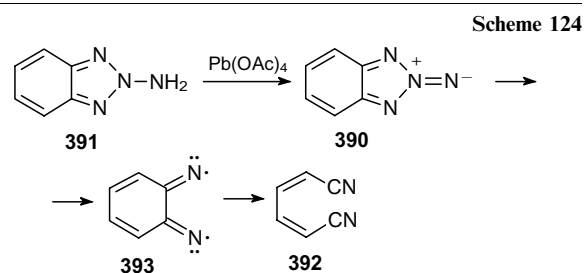
Dichloropyrazines **387** react with NaN_3 in DMF to afford 2,3-diazidopyrazines **388** (Scheme 123).^{235, 236} The IR spectra of these products show no signals of an azido moiety. This fact suggests that 2,3-diazidopyrazines exist in the tetrazole form (**389**) rather than in the diazide one both in solution and in the solid state.



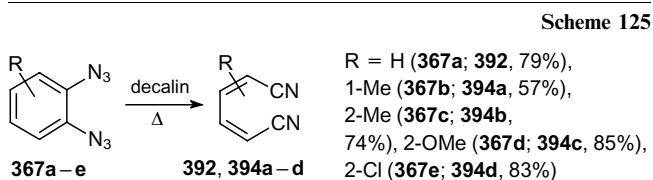
3.4. Reaction of vicinal diazides

3.4.1. Thermal decomposition

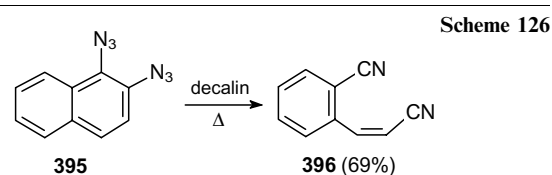
In 1965, Campbell and Rees²³⁷ postulated the existence of compound **390** upon the oxidation of 2-aminobenzotriazole (**391**) with lead tetraacetate. It was proved that it is this compound that is a possible precursor to *cis,cis*-1,4-dicyanobuta-1,3-diene **392**. The N–N bonds of compound **390** are homolytically cleaved to generate diradical **393**, which is then converted to dinitrile **392** due to a homolytic cleavage of the corresponding C–C bond. As a result, the configuration of the aromatic ring system is completely retained (Scheme 124).



In 1967, in view of these findings, Hall and Patterson²²¹ developed an efficient method for the preparation of dicyano derivatives based on the thermal decomposition of 1,2-diazido substituted compounds. Thus, when heated to reflux in decalin, 1,2-diazidobenzenes **367a–e** produce *cis,cis*-1,4-dicyanobuta-1,3-diene (**392**) and its derivatives **394a–d** in high yields (Scheme 125, the positions of the substituents in the product are indicated).

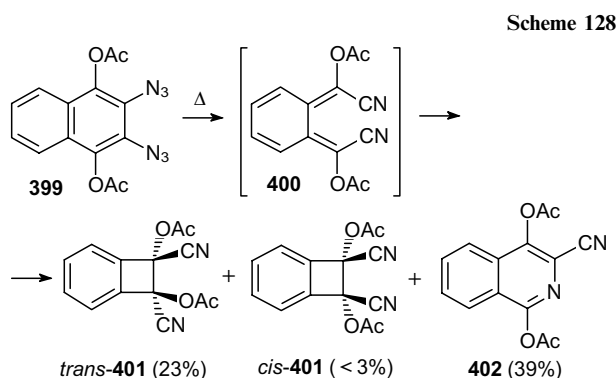
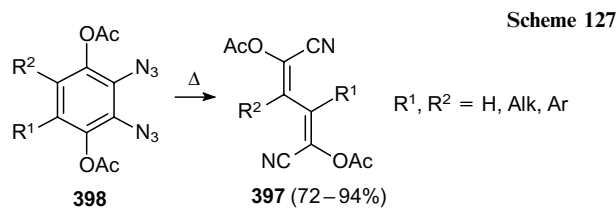


In turn, 1,2-diazidonaphthalene **395** in refluxing decalin gives *cis*-2-(2-cyanovinyl)benzonitrile (**396**) in moderate yield (Scheme 126).

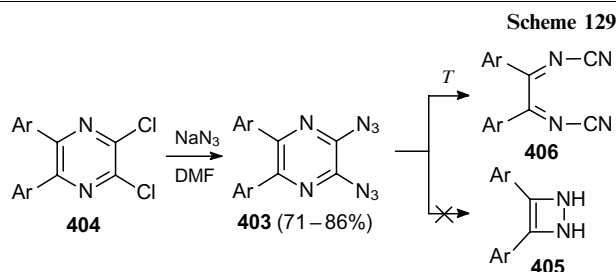


Later, this approach was implemented to synthesize 1,4-diacetoxy-1,4-dicyanobuta-1,3-dienes **397** via aromatic ring cleavage of 1,4-diacetoxy-2,3-diazidobenzenes **398** in refluxing *o*-dichlorobenzene (Scheme 127).²¹⁰

The thermal decomposition of 1,4-diacetoxy-2,3-diazidonaphthalene (**399**) affords intermediate quinodimethane **400** but the electronic and steric effects lead to electrocyclic cleavage of this compound, thereby providing a direct route to the benzocyclobutene ring system. This gives a mixture of isomeric benzocyclobutenes **401** and isoquinoline **402** (Scheme 128).^{210, 238}



Noteworthy are examples of the synthesis and transformations of pyrazines bearing two or more azide moieties, e.g., compounds **403** derived from appropriate dichloro derivatives **404**. While cyclization of azidopyrazines to imidazoles is a well-studied transformation,²³⁹ the possible pyrolytic cyclization of 2,3-diazidopyrazines **403** (see²⁴⁰) into four-membered rings **405** was assumed (Scheme 129). Later,²³⁵ a representative series of such diazides were synthesized, and it was shown that their thermal decomposition affords only dicyanoimines **406**.

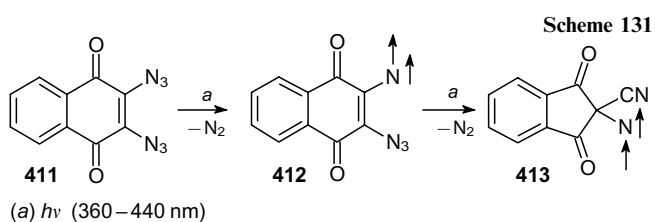
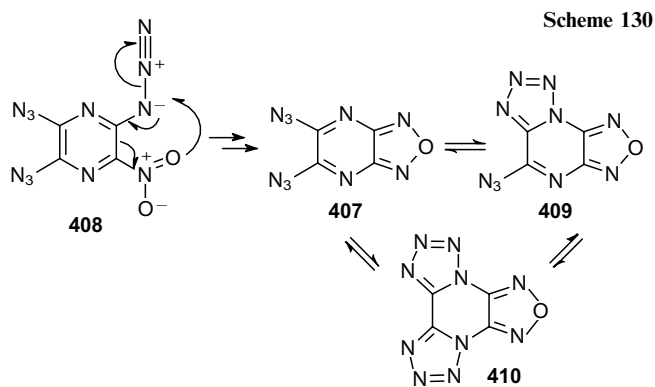


Ar = Ph (52%), 4-BrC₆H₄ (62%), 4-ClC₆H₄ (45%), 4-MeC₆H₄ (56%), 4-MeOC₆H₄ (54%)

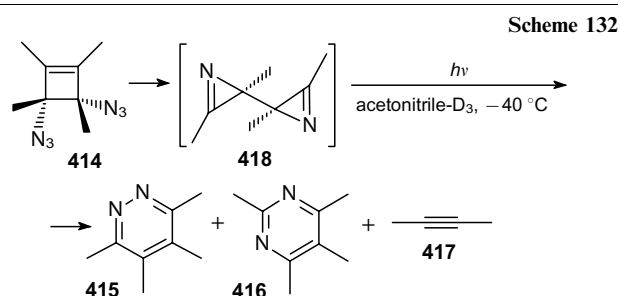
Guillou *et al.*²⁴¹ reported the synthesis of diazidofuranopyrazine **407** from triazidonitropiperazine **408** and the investigation of its tautomerism with forms **409** and **410** using ¹⁵N-labelled atoms (Scheme 130).

3.4.2. Photochemical reactions

Using EPR and IR spectroscopy, it was shown that under cryogenic conditions, irradiation (with a wavelength of 360–440 nm) of 2,3-diazido-1,4-naphthoquinone (**411**) affords vinyl nitrene **412**, which absorbs another photon to form triplet alkyl nitrene **413** (Scheme 131).²¹¹ This process is a striking example of photochemical transformations of 1,2-diazides. Thus, a new method for the preparation of triplet alkyl nitrenes was developed, which have a potential in high-spin assemblies.



In 2001, Banert and Köhler²⁴² showed that the photolysis of *cis*- and *trans*-1,2-diazidocyclobutenes (e.g., compound **414**) in CD₃CN at –40 °C produces a mixture of products **415** and **416** along with a trace amount of alkyne **417**. This process occurs *via* intermediate diazirinyl **418** (Scheme 132).

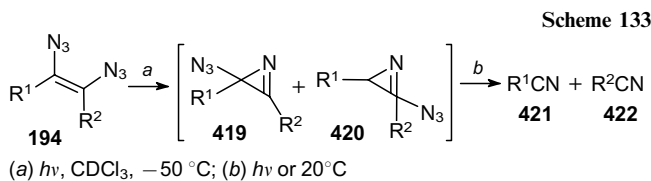


In 2008, it was demonstrated²⁴³ that 2-azido-2*H*-azirines **419** and **420** are intermediates in the photochemical transformation of open-chain 1,2-diazidoethenes **194** to cyano compounds **421** and **422**. Intermediates **419** and **420** were identified by NMR spectroscopy at low temperature. Upon prolonged irradiation or heating, such heterocycles lose a second molecule of nitrogen to form two moieties of the corresponding cyano compounds (Scheme 133).

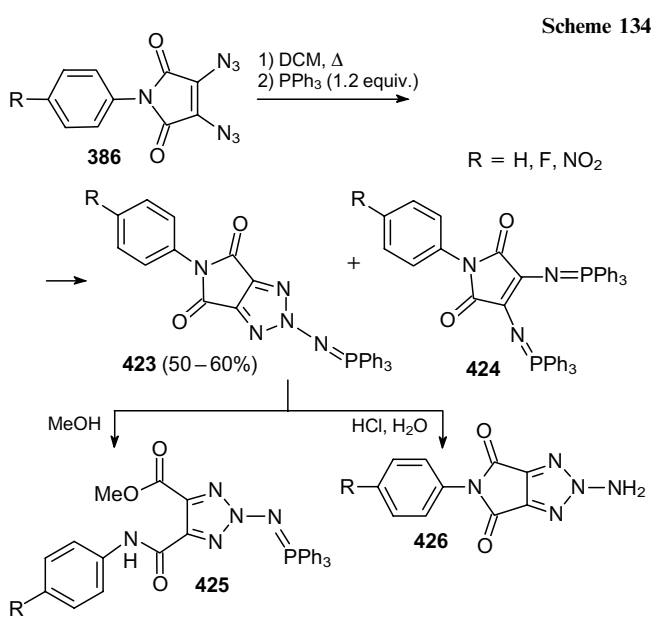
3.4.3. Reactions with organophosphorus compounds

Mao *et al.*²³³ studied the reaction of vicinal diazides of *N*-arylmaleimide **386** with triphenylphosphine (Scheme 134). At room temperature and above, triazole **423** is the major product of this reaction. Also, double Staudinger product **424** is formed in trace amounts, which can readily be obtained at lower temperatures.²⁴⁴ In the presence of methanol or ethanol, compound **423** undergoes a maleimide ring-opening to give the corresponding ester **425**. Upon acid hydrolysis, compound **423** eliminates P(O)Ph₃ and affords the corresponding amine **426**.

In a similar way, triphenylphosphine reacts with naphthoquinone-2,3-diazide **411** derived from dichloride **427** to



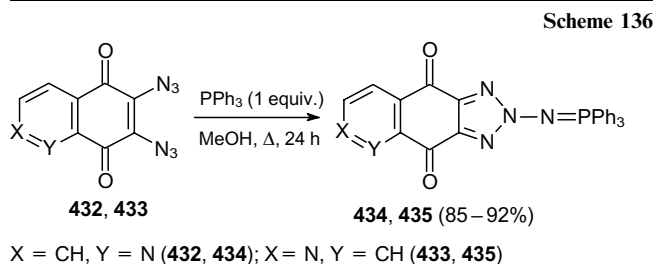
		Yield (%)			
R ¹	R ²	419	420	421	422
CH ₂ S(O)Ph	H	28	39	> 80	> 80
CH ₂ SO ₂ Ph	H	26	34	> 99	> 99
CH ₂ SO ₂ Ph	Me	28	26	> 99	> 99
Ph	CHO	0	43	37	0
4-ClC ₆ H ₄	CHO	33	30	0	0



produce 2-iminophosphorane-1,2,3-triazole **428** in almost quantitative yield.²⁴⁵ In turn, in acidic medium, iminophosphorane **428** is hydrolyzed to free 2-amino-1,2,3-triazole **429**. In the presence of moisture, the reaction of compound **411** with PBU_3^{II} also furnishes product **429** (38%). Diazide **411** also reacts smoothly with bis(diphenylphosphino)methane to form dimer **430** (Scheme 135). The mechanism of

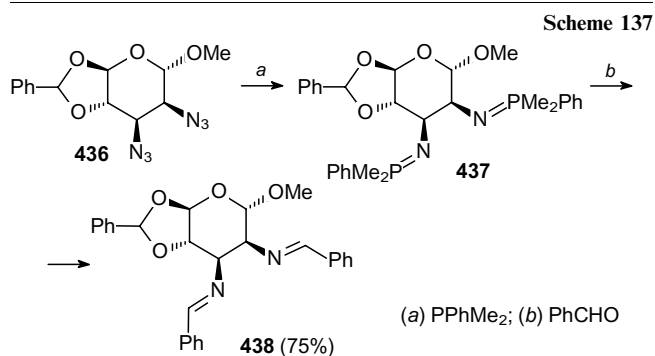
the formation of 2-iminophosphorane-1,2,3-triazole **428** involves the addition of a phosphine molecule to an azide function followed by the elimination of a nitrogen molecule from intermediate **431**.²²³

In a similar way, diazides **432** and **433** can provide an



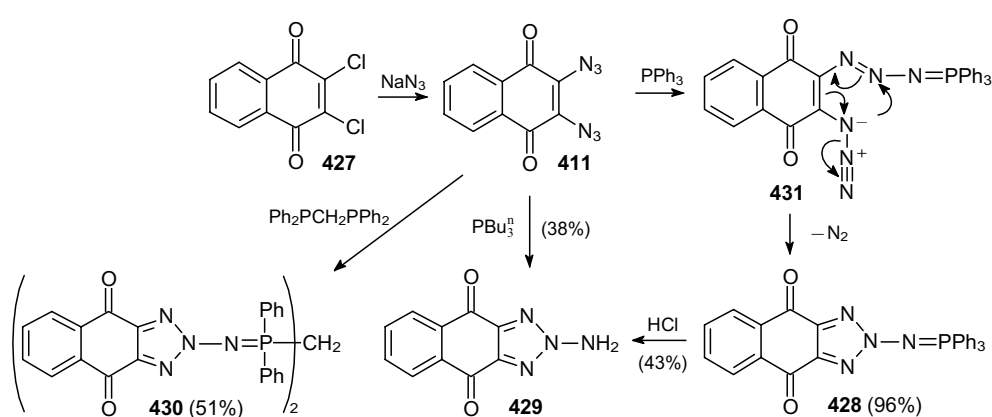
access to (iso)quinolinediones **434** and **35** (Scheme 136).²⁴⁶

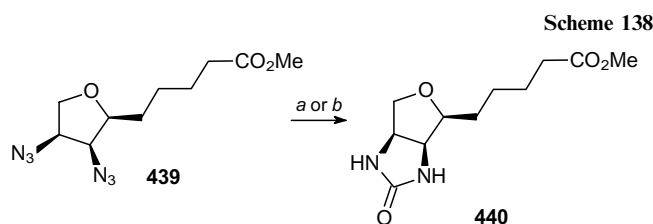
The reaction of an azide moiety with phosphine was used in the synthesis of *N,N*-ligands based on 2,3-diazido-2,3-dideoxy- α -D-mannopyranose.²⁴⁷ Diazide **436** reacted with dimethylphenylphosphine in toluene to afford iminophosphorane **437**. The latter was converted *in situ* to diimine



438 through the reaction with benzaldehyde (Scheme 137).

Diazide **439** was used as a precursor in the synthesis of (+)-oxybiotin (Scheme 138). When treated with PPh_3 and benzyl chloroformate (method *a*), it gave the desired imidazolidinone **440** in low yield. It should be noted that the catalytic one-pot reduction of diazide **439** followed by the treatment with triphosgene (method *b*) significantly improves the yield of the product.^{248, 249} Compound **440**, when treated with barium hydroxide under the hydrolysis conditions, is converted to (+)-oxybiotin.

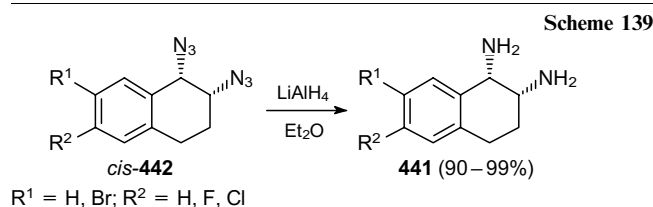




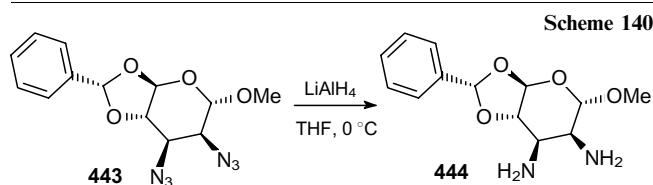
(a) 1) PPh_3 , BnOC(O)Cl , THF, rt, 5 h; 2) NH_4OH , H_2O , rt, 18 h (24%); (b) 1) H_2/PtO_2 , DCM, rt, 6 h; 2) Et_3N , triphosgene reagent, 0 °C, 1 h, rt, 18 h (68%)

3.4.4. Reduction of vicinal diazides to diamines

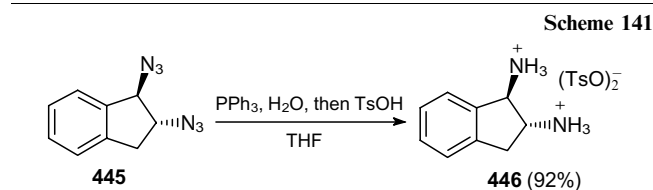
In 1980, Saito *et al.*²⁵⁰ reported the synthesis of potential immunostimulants, hexahydronaphthimidazothiazoles, using *cis*- and *trans*-isomeric 1,2-diamino-1,2,3,4-tetrahydronaphthalenes **441** as key intermediates (Scheme 139). The reduction of azide moieties with LiAlH_4 in diethyl ether makes it possible to convert vicinal diazides **442** to the corresponding diamines in almost quantitative yields.



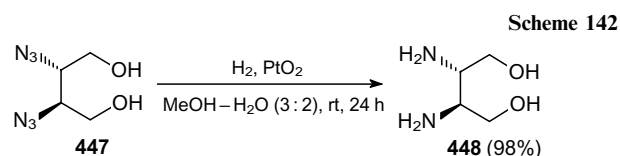
Lithium aluminium hydride was also employed in the final step of the synthesis of methyl-2,3-diamino-4,6-*O*-benzylidene-2,3-dideoxy- α -D-hexapyranoside ligands, in which diazide **443** was reduced to diamine **444** (Scheme 140).^{251–253} In a number of studies,^{254–256} the similar protocol was applied to reduce vicinal diazides.



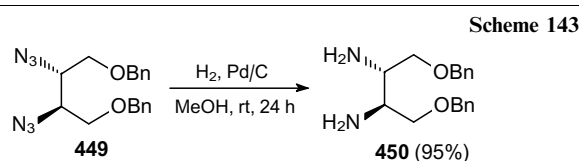
In 2017, (\pm)-*trans*-1,2-diazidoindane (**445**) was used to prepare the corresponding diamine.¹⁹¹ The reduction using the $\text{PPh}_3\text{-H}_2\text{O}$ system and *p*-toluenesulfonic acid allowed the preparation of *trans*-indene diaminium salt **446** in 92% yield (Scheme 141).



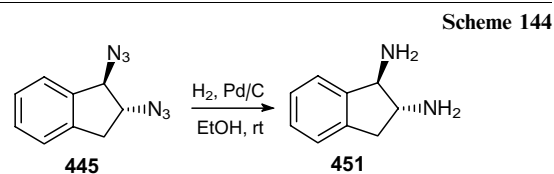
The catalytic hydrogenation of azide moieties in compound **447** in the presence of Adams catalyst (PtO_2) in a H_2 atmosphere gives bis(amino alcohol) **448** in nearly quantitative yield (Scheme 142).^{34, 137, 160, 162, 249}



In this case, Adams catalyst is more preferable compared to such systems as Pd/C and Pearlman's catalyst [$\text{Pd}(\text{OH})_2/\text{C}$], which provide modest yields of the product (20–30%). The protection of hydroxy groups significantly affects the reaction outcome. Thus, *O*-benzylated diazide **449** is reduced over Pd/C to diamine **450** in quantitative yield (Scheme 143).²⁵⁷



The catalytic reduction of (\pm)-*trans*-1,2-diazidoindane **445** with hydrogen in the presence of palladium on carbon in anhydrous ethanol gives (\pm)-*trans*-1,2-diaminoindane **451** in quantitative yield (Scheme 144).²⁵⁸ In general, this method of reduction of diazides is suitable for a wide range of diazides and its application is well documented in the literature (see, *e.g.*, Refs 259–267).



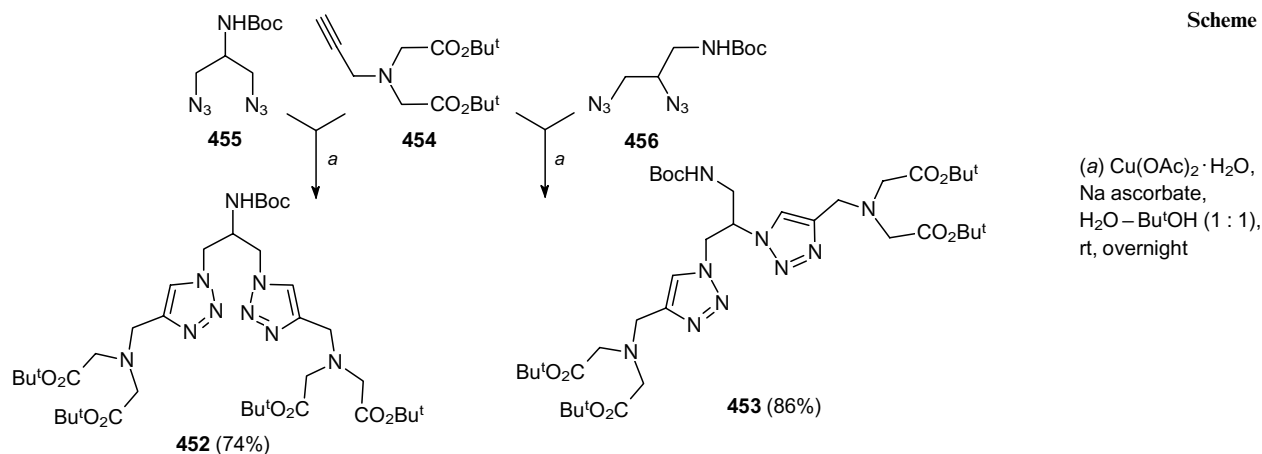
3.4.5. Azide–alkyne [3 + 2]-cycloaddition. Bis(triazoles)

Using classical click chemistry conditions,²⁶⁸ a versatile synthetic approach has recently been developed to prepare bifunctional chelating agents **452** and **453**, which are bis(triazole)-based polyaminocarboxylic acids. Thus, the azide–alkyne cycloaddition catalyzed by the $\text{Cu}(\text{OAc})_2$ –sodium ascorbate system provides the synthesis of the target bis(triazoles) **452** and **453** in high yields from alkyne **454** and diazides **455** and **456**, respectively (Scheme 145).

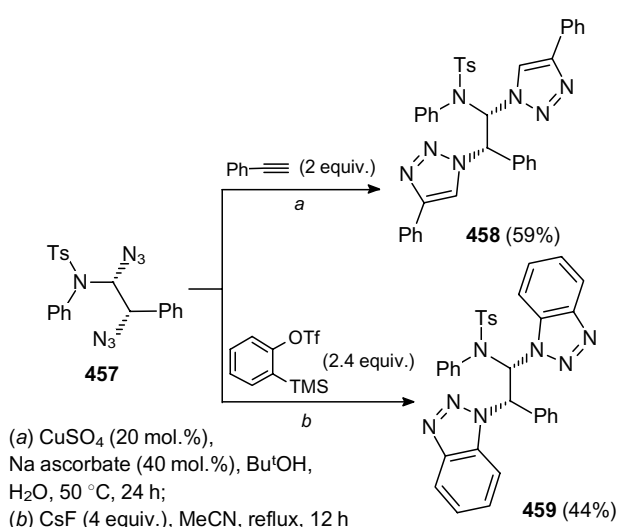
This catalytic system is more preferable than the CuI –diisopropylamine system. Instead of catalysts based on $\text{Cu}(\text{OAc})_2$, the CuSO_4 –sodium ascorbate system is often used.^{200, 269–275} Thus, *via* the Cu -catalyzed double [3 + 2]-cycloaddition involving phenylacetylene, *cis*-diazide **457** gives 1,4-disubstituted *cis*-bis(triazole) **458** in 59% yield (Scheme 146).¹⁸⁴ Diazide **457** can be converted to the corresponding bis(benzotriazole) **459** in 44% yield. The latter case is a non-catalytic version of the [3 + 2]-cycloaddition, where an alkyne component is formed *in situ* during the reaction. Similar procedures were described in the publication.¹⁸⁶

It was demonstrated that 1,2-diazides **460** and **461**, derived from glycals, can be subjected to [3 + 2]-cycloaddition. Thus, the corresponding bis(triazoles) **463** and **464** were obtained in high yields using phenylacetylene or carbohydrate **462** bearing a terminal alkyne moiety (Scheme 147).¹⁸⁵

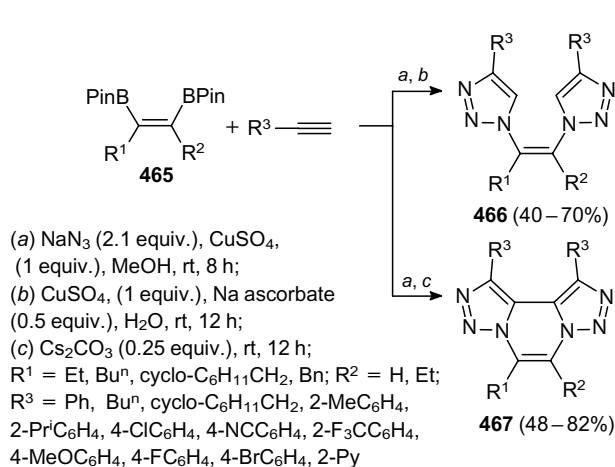
Scheme 145



Scheme 146



Scheme 148

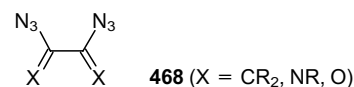


Mali *et al.*²⁰⁰ described the synthesis of vicinal *cis*-diazidoalkenes from 1,2-diboronate ester pinacol boronates **465**. Because of instability of such diazidoalkenes, they were generated *in situ* using sodium azide and the CuSO_4 –sodium ascorbate catalytic system. As a result, bis(triazolo)pyrazines **466** were obtained (Scheme 148). It should be noted that modifying the reaction conditions and switching to another catalytic system provide a convenient route to bis(triazolo)pyrazines **467**, a new class of fused heterocycles. This approach to bis(triazolo)pyrazines stimulates the formation of five bonds at once in a single reaction step while retaining all atoms present in the substrates.

3.5. Vicinal diazidodienes and their heteroanalogues

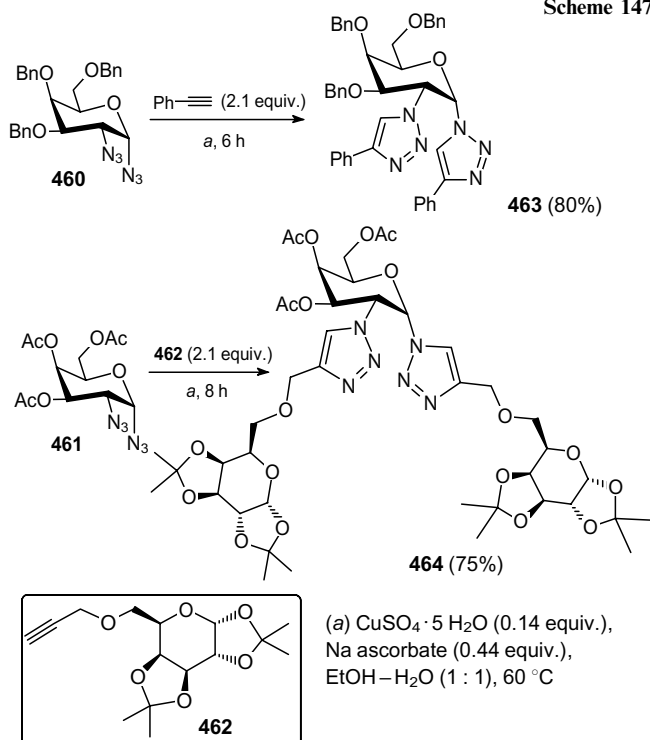
The main classes of diazides related to compounds of this type can be represented by the general formula **468**. Examples of each class are considered below.

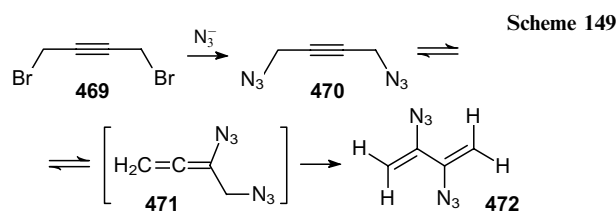
Structure 468



The synthesis of butadienes bearing azide functionalities at the positions 2 and 3 is mentioned in publications.^{276, 277} 1,4-Dibromobut-2-yne (**469**) was used as a starting compound, which reacted with an azide ion to give first bis(diazidomethyl)acetylene (**470**), being in equilibrium

Scheme 147

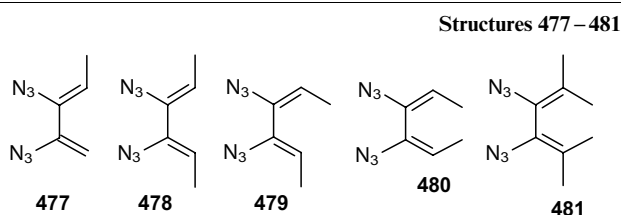




with allene **471**, and then 2,3-diazidobuta-1,4-diene (**472**) (Scheme 149). Structural features of diazidobutadienes were studied in 1986, soon after the first report about the possibility of the synthesis of such compounds.^{278, 279}

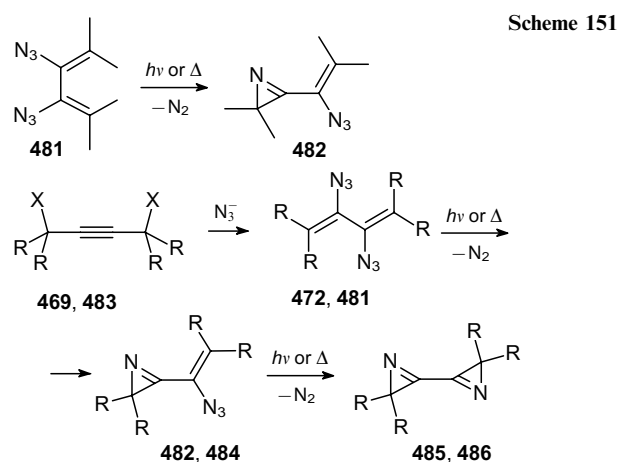
The [4+2]-cycloaddition of a variety of compounds acting as dienophiles to diene **472** was investigated by Banert.^{280, 281} Scheme 150 illustrates the examples of transformations involving 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione and tetracyanoethylene, resulting in the formation of adducts **473** and **474**, which eliminate two nitrogen molecules under photochemical or thermal conditions to furnish products **475** and **476**.

In the same publications, the reactivity of homologues of diazidobutadiene **477–481** in the [4+2]-cycloaddition reaction was studied.



In the case of isomers and homologues **477–479**, the [4+2]-cycloaddition to tetracyanoethylene occurs similar to that depicted in Scheme 150, while no reaction is observed for compound **480** (*E,E* isomer). Homologue **481** bearing four methyl groups is not involved in [4+2]-cycloaddition; however, under these conditions, partial intramolecular cyclization of diazidodiene into azirine **482** occurs. The synthesis of azirines from diazidobutadiene was first reported by Banert in 1985.²⁸² Two years later, this type of reactions, typical of unsaturated azides, was described in details.²⁸³ Scheme 151 represents the general sequence of thermal or photochemical destruction of diazidodienes **472** and **481** derived from dihalides **469** and **483**. As a result, mono- (**482**, **484**) and diazirines (**485**, **486**) were obtained.

The synthesis of dicarbonyl diazide (oxalyl diazide) **488** from oxalyl dihydrazide **487** and its high explosive sensitivity were first described in 1964.²⁸⁴ In the same publication, selected chemical properties of compound **488** are considered, in particular its conversion to azidocarbonyl isocyanate **489** accompanied by the loss of one nitrogen molecule. The reaction of azide **489** with ethanol affords compound **490**, with an azide moiety being intact (Scheme 152). More



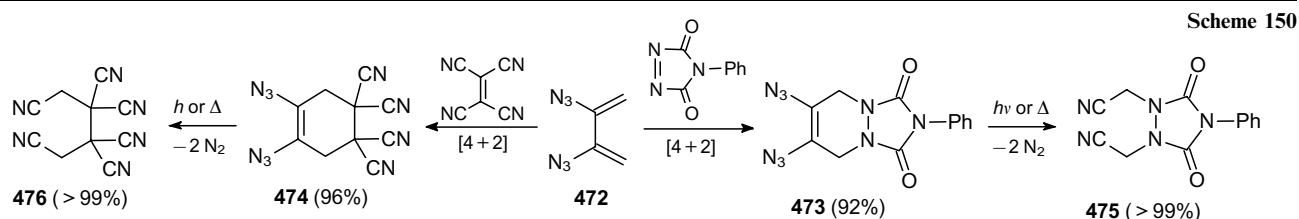
X = Cl, Br; R = H (**469**, **472**, **484**, **485**), Me (**481–483**, **486**)

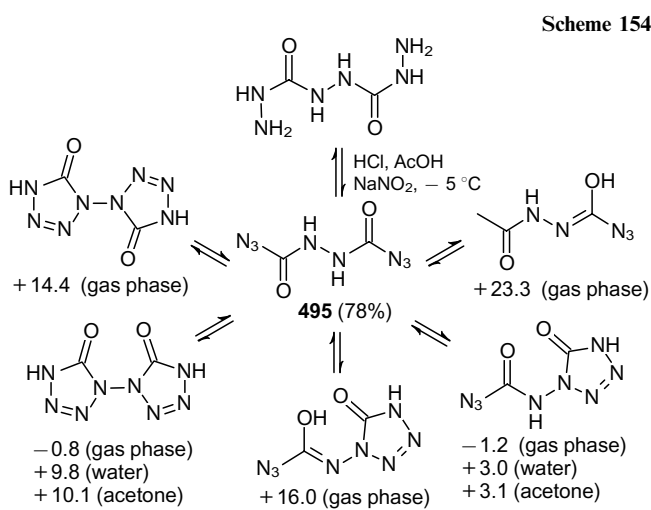
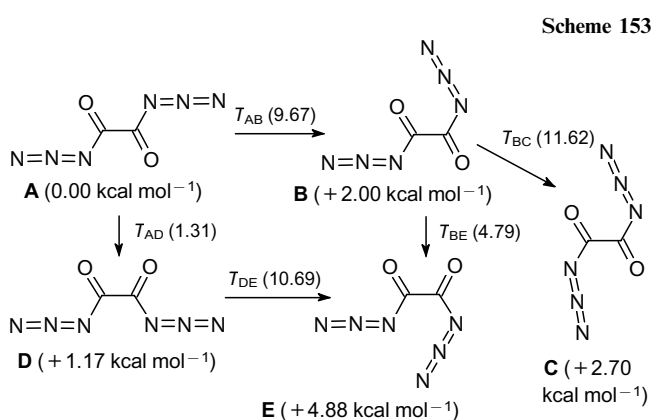
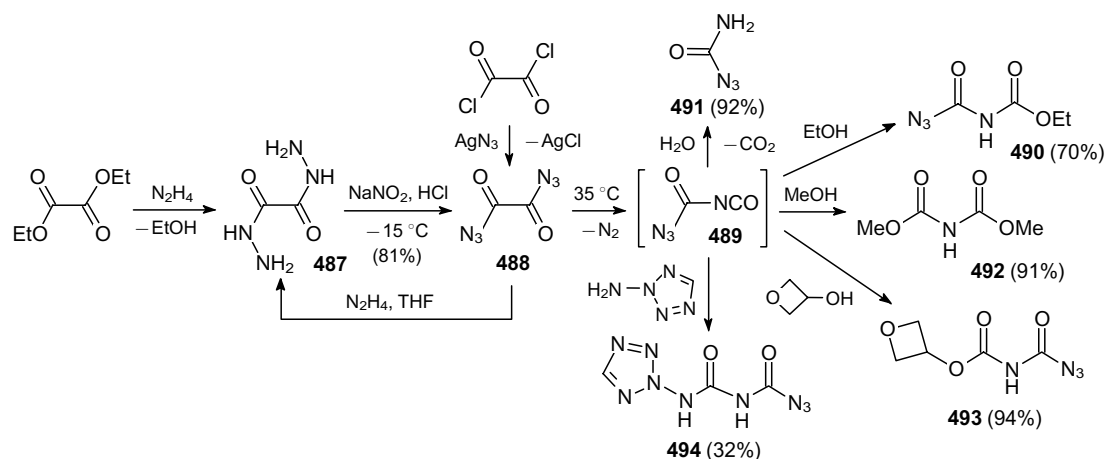
than 40 years later, diazide **488** was prepared by passing oxalyl chloride vapour through a tube filled with the freshly prepared silver azide.²⁸⁵ The product was not isolated but just identified by photoelectron spectroscopy. Harter *et al.*²⁸⁶ studied in detail the chemical properties of intermediate compound **489** formed *via* the thermal decomposition of oxalyl diazide **488**. When carrying out this reaction in protic solvents, the newly formed isocyanate **489** reacts with moist air or solvent to give product **491** in high yield. The reaction with hydroxy-containing compounds can involve either one or both azide moieties to form the corresponding products **492** and **493**. This strategy was extended to compounds bearing an amino functionality. For example, the reaction of azide **489** with aminotetrazole affords azide **494** though in low yield.

For oxalyl diazide **488**, quantum chemical calculations were carried out (DFT, B3LYP/6-311 + G(3df)) and the transition energies between its possible A–E conformers were calculated (Scheme 153; the relative energies of the conformers are given in parentheses under the structures; the energies of the transition states are given in parentheses above the arrows). According to the calculations, conformer **A** is the most energetically favourable, the energy of its transition to the **D** form is as low as 1.31 kcal mol⁻¹.

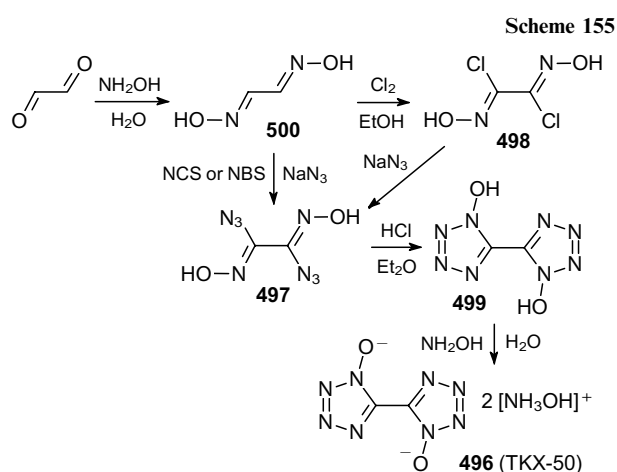
Also reported²⁸⁶ is the synthesis of diazide **495** containing the N₃C(O)NHR structural motif (Scheme 154). The results of the study of chemical properties of this diazide were not considered, but the energies of possible tautomeric forms of this compound were assessed (given under the formulas in kcal mol⁻¹), the stability of this compound was evaluated to be higher than that of oxalyl diazide **488**.

Worthy of special attention are studies aimed at developing efficient and safe methods for the production of the TKX-50 explosive (Structure **496**, Scheme 155). This compound is most commonly synthesized from glyoxal using multistep methods, which involve the preparation of diazidoglyoxime **497** as a key step. Chlorine atoms of com-





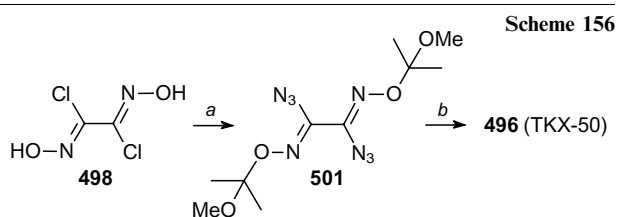
compound **498** are very effectively replaced due to the presence of activating substituents. When studying this reaction, Tselinskii *et al.*²⁸⁷ observed the solvent effect. Thus, in acetone or acetonitrile, the diazide is formed in ~50% yield; in aqueous ethanol, the yield is 76%; in DMF, it is nearly quantitative. Then diazide **497** undergoes tautomerization in an acidic medium to bis(hydroxytetrazole) **499**, which can form salts with alkali and alkaline earth metals,²⁸⁸ ammonium²⁸⁹ or hydroxylamine to afford the target explosives.^{290, 291} Patents^{292, 293} address the possibility of combining two intermediate steps into one by using *N*-halogenated succinimides as halogenating agents for dioxime



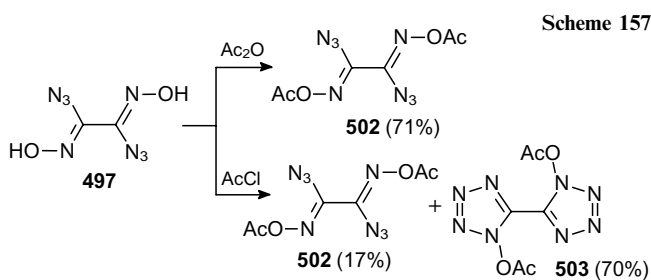
500 (see Scheme 155). Besides DMF, DMSO and *N*-methyl-2-pyrrolidone are also suitable solvents for this transformation.

In 2018, the thermal stability of intermediates and TKX-50 was studied using thermogravimetric analysis and differential scanning calorimetry and also the corresponding quantum chemical calculations.²⁹⁴ The safety of the synthetic protocol for compound **496** can be enhanced by adding one more intermediate step, namely, the preliminary protection of hydroxyl groups of dihydroxyglyoxime immediately prior to the replacement of chlorine atoms by azide moieties. In most cases, the tetrahydropyranyl protection is used for this purpose.^{295–298} However, in 2021 it was proposed²⁹⁹ to protect OH functionalities with 2-methoxyprop-1-ene and to isolate intermediate diazide **501** (Scheme 156).

Diazidoglyoxime **497** can be acylated by the treatment with acetic anhydride or acetyl chloride.²⁸⁷ In the latter

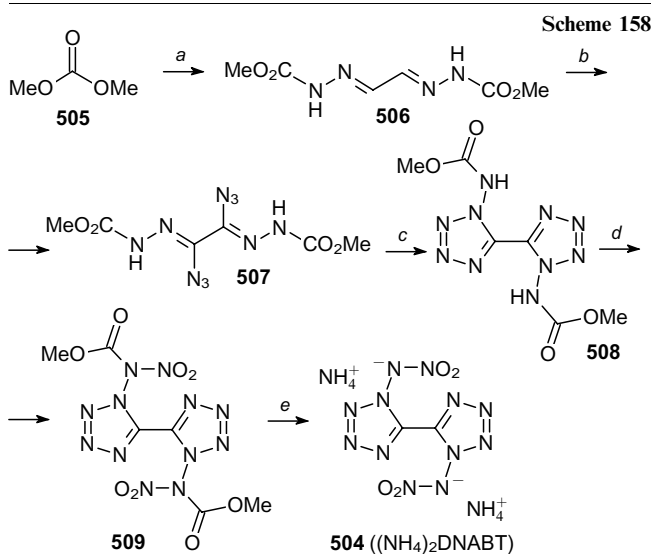


(a) 1) protection, 2) azidation; (b) 3) deprotection and cyclization, 4) salt formation



case, a mixture of diacetylated diazidoglyoxime **502** and bis(tetrazole) derivative **503** was obtained as a major reaction product (Scheme 157).

Over the past decade, publications have emerged on the synthesis of 1,1'-dinitramino-5,5'-bis(tetrazole) (DNABT, **504**) (Scheme 158), its salts and derivatives, which are explosives.^{300–303} The complete scheme for the synthesis of diammonium salt of DNABT from dimethyl carbonate (**505**), hydrazine and glyoxal was reported in the study.³⁰¹ Diazobutadiene **506** and diazide **507** were isolated as intermediates, the latter compound being cyclized into bis(tetrazole) derivative **508** in an acidic medium. Its nitration gives compound **509**, which is transformed into product **504**. A similar scheme is used to prepare dipotassium salt of DNABT.³⁰³



(a) 1) N_2H_4 ; 2) glyoxal (0.5 equiv.); (b) 1) NCS, DMF; 2) NaN_3 , DMF; (c) HCl, Et_2O ; (d) N_2O_5 , MeCN; (e) NH_3 (aq.)

4. Organic tri-, tetra- and polyazides. Synthesis, properties and application

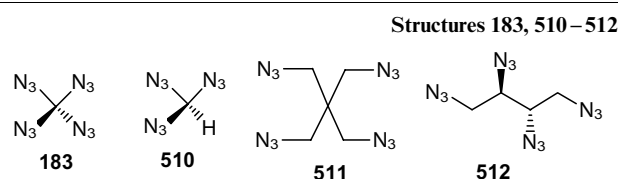
Cationic triazide $\text{C}(\text{N}_3)_3^+\text{SbCl}_6^-$ was first synthesized in 1966.³⁰⁴ Using IR spectroscopy, it was established that the newly formed triazidocarbenium cation $\text{C}(\text{N}_3)_3^+$ has C_{3v} -symmetry, with the central carbon atom lying in the same plane with three neighbouring nitrogen atoms. The cationic part of this compound is isoelectronic with diazide $\text{NC}-\text{N}=\text{C}(\text{N}_3)_2$, which can be prepared from sodium azide and cyanogen bromide (BrCN).¹³⁰ The triazidocarbenium cation $\text{C}(\text{N}_3)_3^+$, being highly endothermic, forms the corresponding energetic salts with such anions as $\text{N}(\text{NO}_2)_2^-$ and ClO_4^- . Also, the salt $\text{C}(\text{N}_3)_3^+\text{BF}_4^-$ was prepared.³⁰⁵ Electronic structure calculations carried out for

the $\text{C}(\text{N}_3)_3^+$ cation showed that in all cases the planar structure with C_{3v} symmetry has the minimum energy. The heats of formation of $\text{C}(\text{N}_3)_3^+\text{N}(\text{NO}_2)_2^-$ and $\text{C}(\text{N}_3)_3^+\text{ClO}_4^-$ were evaluated as endothermic with values of 252 and 218 kcal mol^{-1} , respectively, which explains the high explosiveness of these compounds. Despite the fact that the sensitivity of triazidocarbenium salts to heat and impact is too high for practical use, such compounds represent a new class of materials with high-energy density and demonstrate that endothermicity up to 1 kcal g^{-1} is quite achievable for ionic solids.

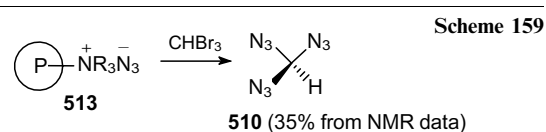
As for organic tri-, tetra- and polyazides, aliphatic, alkenyl and aromatic representatives of this class of compounds are known to date.

4.1. Aliphatic tri-, tetra- and polyazides

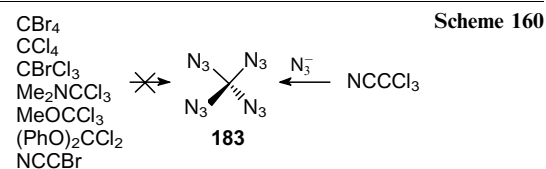
Among alkyl derivatives of polyazides, structures **183**, **510–512** deserve attention.



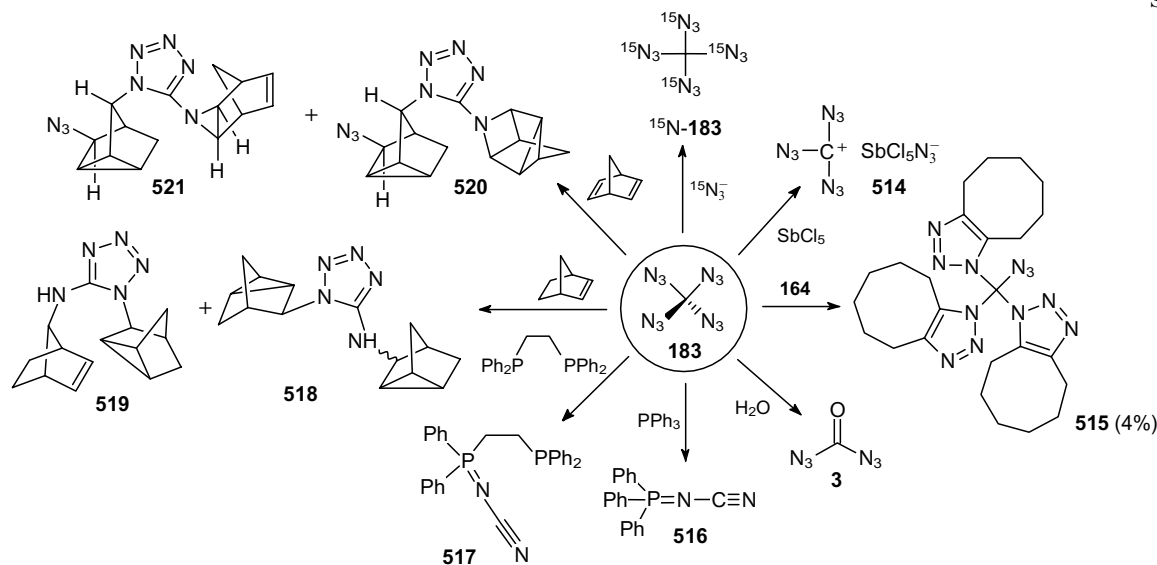
Triazidomethane (**510**) was first mentioned by Hassner *et al.*³⁰⁶ in 1990. The procedure for the preparation of this compound from bromoform involves the replacement of bromine atoms with azide groups using azide-containing polymer **513**, which was prepared from the anion exchange resin Amberlite IR-400 and sodium azide (Scheme 159). It is important to note that the authors of the cited study did not use an individual compound but an ethereal solution of a mixture of the starting bromoform and supposedly triazidomethane, taking diethyl ether : CHBr_3 : **510** in the 10 : 34 : 35 ratio. The formation of the product was confirmed by gas chromatography and NMR spectroscopy; the transfer of this solution into the ampoule may cause an explosion.



More than 25 years later, in 2007, Banert *et al.*¹²⁶ reported the results of the synthesis and studies on the chemical properties of tetraazidomethane (**183**). A variety of the starting halogenated organic reagents were tested but the desired tetraazidomethane was isolated only using trichloroacetonitrile (Scheme 160). Unfortunately, the authors did not report the yield of tetraazide **183** but noted that the resulting compound is highly explosive. Nevertheless, this tetraazide was characterized by ^{15}N NMR spectroscopy and was shown to have rich chem-



Scheme 161



istry. Thus, it can give rise to products **3**, ^{15}N -**183** and **514–521** (Scheme 161).

Tetraazide **183** reacts with antimony pentachloride to form salt **514**, in which the above-mentioned triazidocarbenium cation acts as a cation. Also worthy of note are the hydrolysis of tetraazidomethane to diazidophosgene (**3**), its reactions with phosphorus(III) compounds to afford cyanophosphazenes **516** and **517**, respectively, and also the cycloaddition involving norbornene and dicyclopentadiene to form disubstituted tetrazoles **518–521**. Tetraazide **183** can be detected using cyclooctyne (**164**) as a molecular trap ‡ to

‡ This azide–alkyne cycloaddition reaction promoted by strained cycloalkynes is abbreviated as SPAAC (strain-promoted azide–alkyne cycloaddition).

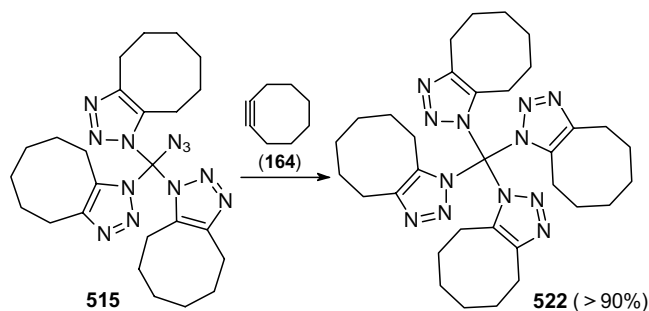
yield stable tris(tetrazole) **515**. The subsequent reaction of the latter compound with cyclooctyne (**164**) leading to the corresponding tetrakis(tetrazole) **522** (Scheme 162) is also possible.¹²⁶

In turn, the reaction of tetraazidomethane with norbornene and dicyclopentadiene affords mixtures of aminotetrazole derivatives. Using the reaction with norbornene, the reaction pathway for chemical transformations occurring under these conditions was proposed (Scheme 163).¹²⁶

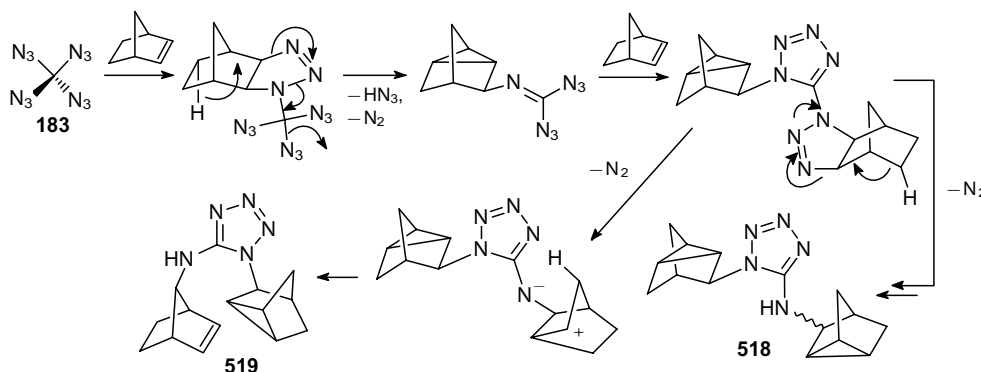
Lyssenko *et al.*³⁰⁷ studied the structural features of pentaerythrityl tetraazide (**511**). They showed that the formation of short contacts between azide moieties in crystals is not typical of this polyazide. Therefore, the assembling of molecules in the solid state for such rigid molecular framework gives rise to a structure with high impact sensitivity, since even small deformations of the crystal structure cause shortening of favourable intermolecular contacts. The synthesis of several azido-containing pentaerythritols is presented in a patent.³⁰⁸ Polynitramine compounds based on tetraazide **511** were produced. In particular, pentaerythrityl tetranitramine **526** was obtained via the formation of derivatives **523–525** (Scheme 164).³⁰⁹ Compound **526** has high density and thermally decomposes at 183 °C; its chemical, thermal and calculated detonation properties were described.³⁰⁹

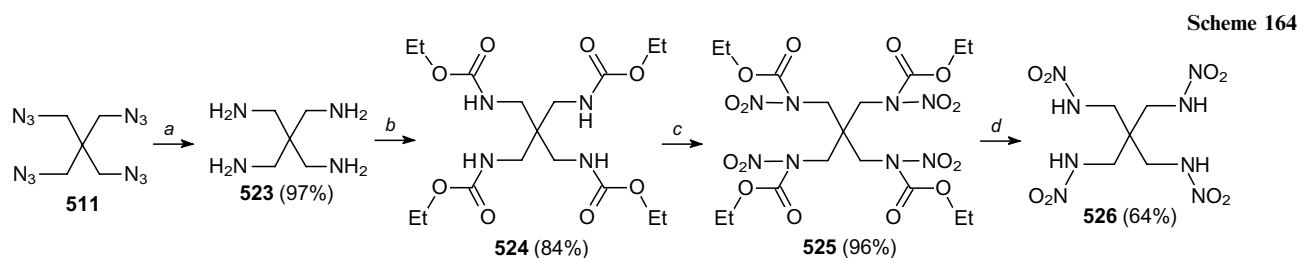
Azide and nitrate derivatives of pentaerythrytol **527–530** were prepared in good yields based on the azide exchange of appropriate bromo derivatives. Tetraazide **511**

Scheme 162



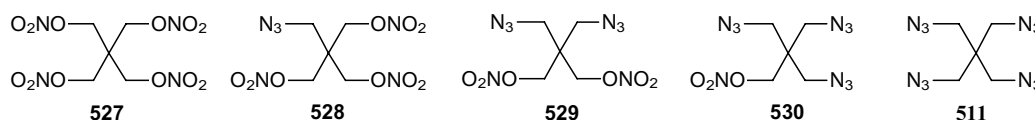
Scheme 163





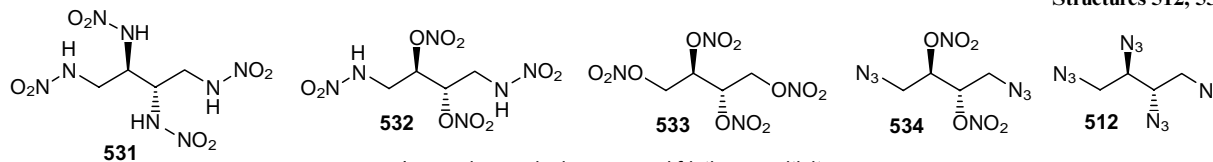
(a) H_2 , Pd/C; (b) EtOC(O)Cl ; (c) HNO_3 , $(\text{CF}_3\text{CO})_2\text{O}$; (d) 1) aq. NH_3 ; 2) 36% HCl

Structures 511, 527–530



Increasing thermal stability and explosiveness

Structures 512, 531–534



Increasing explosiveness and friction sensitivity

was the most stable in this series.³¹⁰ Thermal stability of organic nitrates is limited to 180 °C, while this tetraazide is stable up to 218 °C. The study showed that organic azides are potential candidates for use as novel initiating or melt cast explosives although their thermal or mechanical properties are generally insufficient for practical applications.

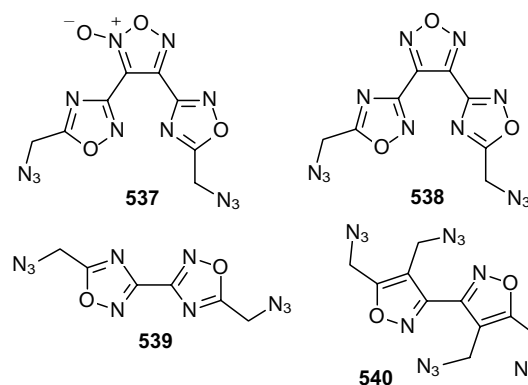
This approach, involving a combination of different functional groups in one molecule, makes it possible to tune the chemical and physical properties of organic compounds. It can help, for example, in the development of novel explosives, the specifications of which are based on certain characteristics of the substance.³¹¹ Thus, an interesting pattern of changes in the properties of compounds **512**, **531–534** is given below.

The synthesis of a number of nitro- and azido-function-alized compounds for their possible use as energetic plasticizers was described in the study.³¹² Tetraazide **535** can be prepared in four steps from glycolic acid; in the final step,

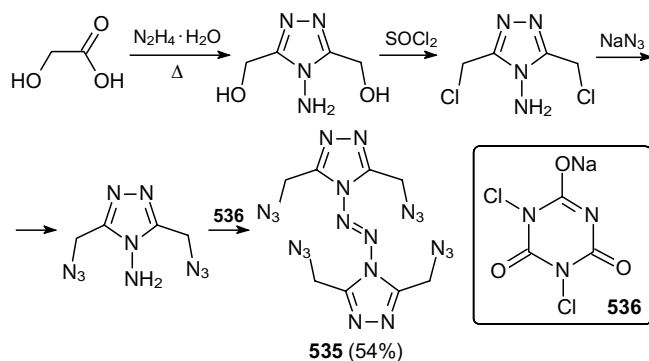
the dimerization is carried out in the presence of triazine **536** (Scheme 165).

Four novel polyazidomethyl structures **537–540** based on heterocyclic compounds were prepared and characterized.³¹³

Structures 537–540

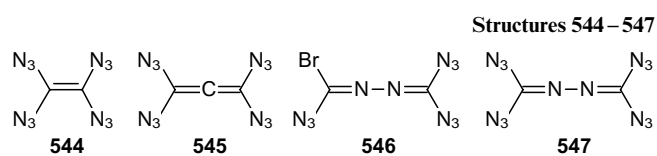
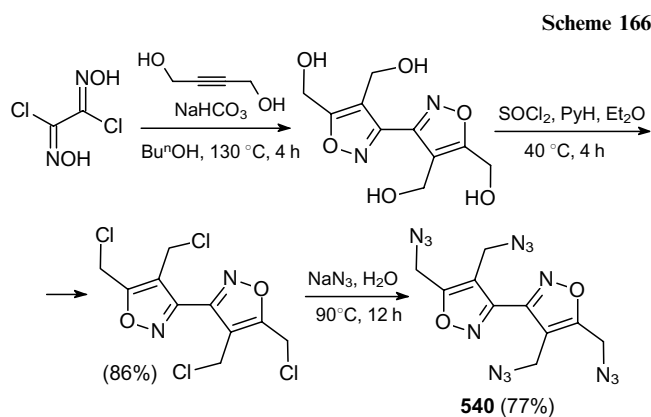


Scheme 165



Compounds **537**, **538** and **540** possess suitable properties as energetic plasticizers. The synthesis of tetraazide **540** from dichloroglyoxime deserves attention (Scheme 166). In the final step, chlorine atoms are replaced with azide moieties.

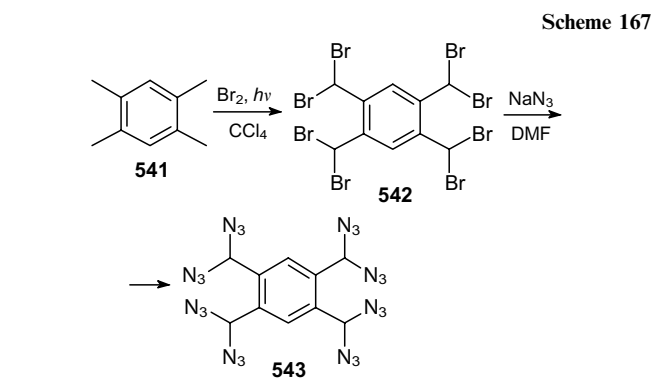
The synthesis from 1,2,4,5-tetramethylbenzene **541** through the formation of polybromide **542** afforded 1,2,4,5-tetrakis(diazidomethyl)benzene (**543**), which was studied by X-ray diffraction analysis (Scheme 167).³¹⁴ This compound appeared to be more stable in the solid state than



compound (Scheme 168).³¹⁶ The treatment of the latter compound with two equivalents of sodium nitrite under acidic conditions affords diazide **550**, which undergoes spontaneous cyclization to 5-azido-1-aminotetrazole (**551**).³¹⁷ The treatment with an aqueous solution of sodium hydroxide leads to the dimerization of salt **550**.³¹⁶ Therefore, dimer **552** bearing four azido moieties is a precursor to triazide **548**. The structures of triazide **548** and the product of its reaction with HCl, compound **553**, were confirmed by spectroscopic methods and X-ray diffraction analysis.

In 2013, Banert *et al.*³¹⁸ reported the synthesis of triazide **548** from tetrabromide **554** according to a known procedure.³¹⁹ Besides, the authors converted this triazide to tetrazole derivative **555** with the use of cyclooctyne (**164**) (Scheme 169). Triazide **548** unexpectedly turned out to be more reactive as compared to its tetraazide precursor **547**.

In 2014, a representative series of a novel class of geminal acyl triazides **556** with various substituents at the carbonyl centre was prepared (Scheme 170).³²⁰ Three simple approaches were proposed to synthesize such triazides, namely, starting from 3-oxocarboxylic acids (method *a*) iodomethyl ketones (method *b*) and terminal olefins (method *c*). Actually, all three proposed methods are variants of an oxidative azidation using a sulfonylated derivative of 2-iodoxybenzoic acid (**45**) and NaN₃ as the azide source. The methods *b* and *c* have proven most effective and provided the synthesis of the target products in yields from 30 to 77% and from 32 to 48%, respectively. Despite a high nitrogen content, geminal triazides are easy to handle when carrying out the synthesis on a preparative scale and are potentially valuable building blocks for the synthesis of amino acids.



expected. It is of interest both for high-energy experiments and as a precursor for the synthesis of carbon nanotubes, nanospheres and high-nitrogen carbon nitrides with great potential in biological and technological applications.

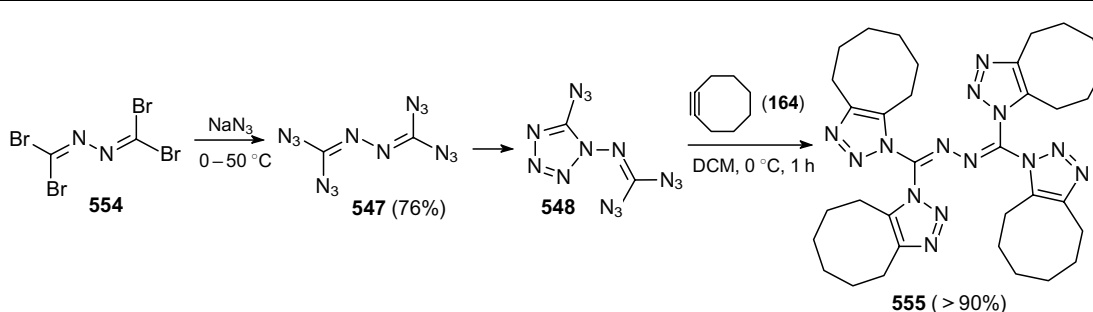
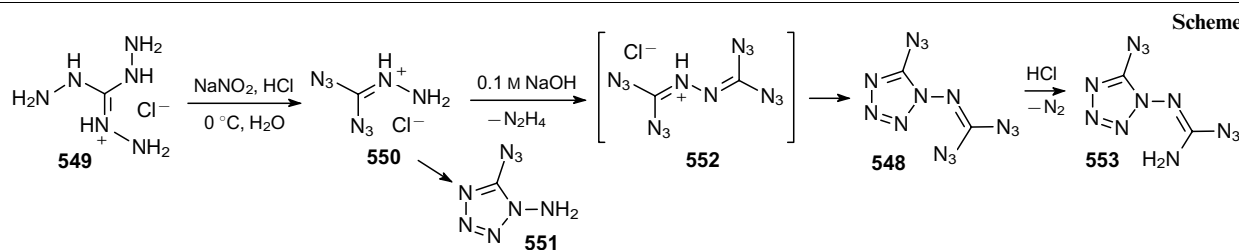
4.2. Alkenyl and carbonyl tri-, tetra- and polyazides

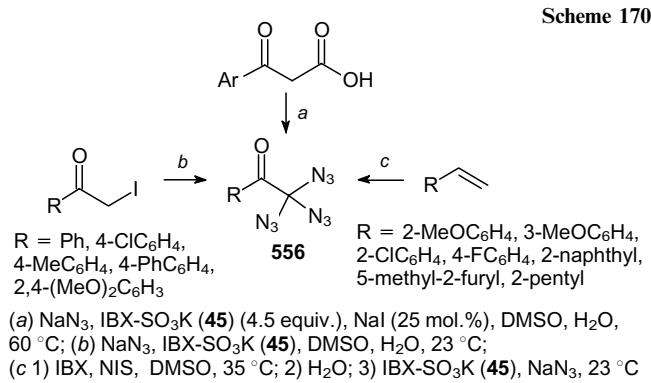
Alkenyl tri- and tetraazides **544–547** were studied by quantum chemical calculations and their structures were optimized; however, these compounds were not synthesized.³¹⁵

It was shown that triazide **548** can be synthesized using triaminoguanidinium chloride (**549**) as the starting com-

4.3. Aromatic and heterocyclic tri-, tetra- and polyazides

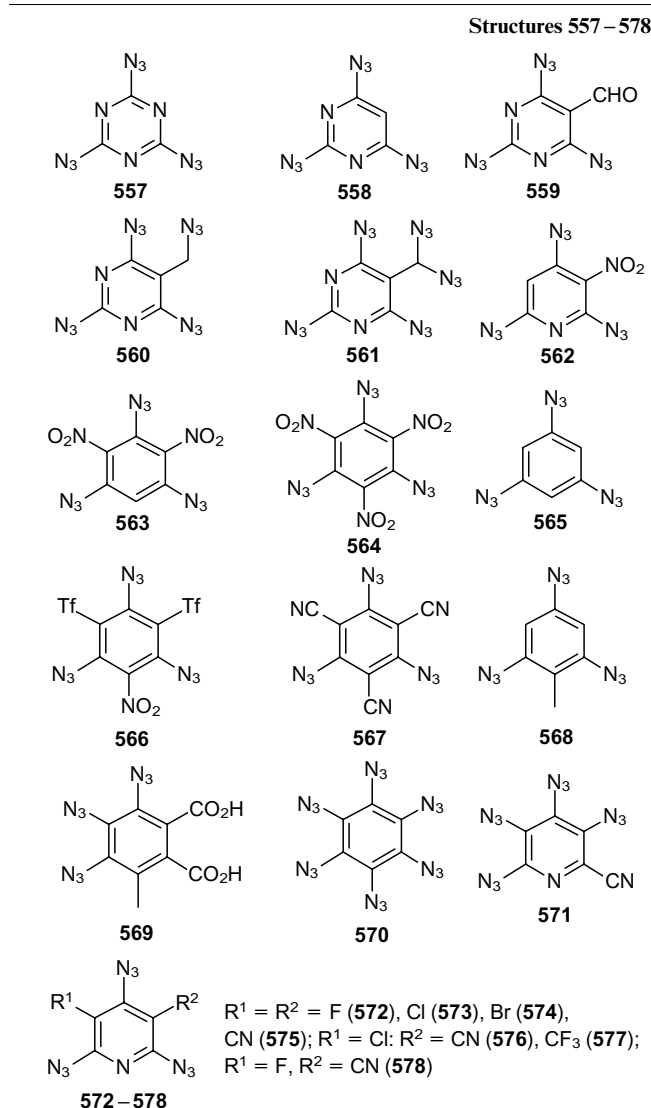
The preparation and chemical transformations of heterocyclic monoazides are discussed in detail in the review.²²





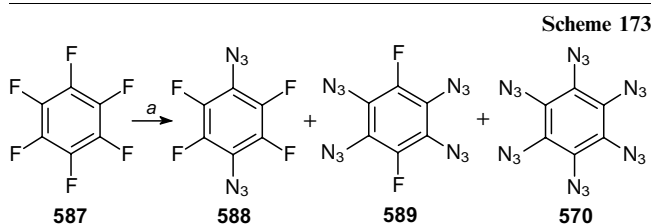
The reviews by Chapyshev^{321,322} address the synthesis, chemical transformations and possible applications of six-membered aromatic azides **557–574** bearing three or more azide moieties in the ring.

These compounds are widely used as the starting materials in organic synthesis and photochemical research and also as photoresistors in microelectronics and crosslinking agents in polymer chemistry. Some aromatic polyazides show high antitumour activity, while the other are of significant interest as energetic compounds and precursors



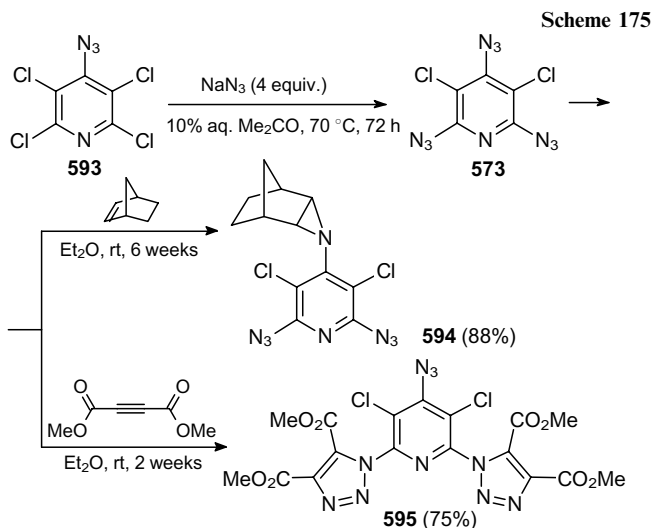
mer industry, as well as the starting materials for preparing organic materials with magnetic properties.

It should be noted that hexafluorobenzene (**587**) reacts with an excess of sodium azide in DMSO at room temperature to produce a mixture of diazide **588**, tetraazide **589** and hexaazide **570** (Scheme 173). For this reason, the azidation of hexafluorobenzene **587** or its hexachloro- and hexabromo-substituted analogues cannot be considered as an approach to the preparation of 1,3,5-triazidobenzenes.³²⁸ Photolysis of halo- and cyano-containing 2,4,6-triazidopyridines in cryogenic matrices was also studied.³²⁹



2,4,6-Triazido-1,3,5-tricyanobenzene (**590**) was first mentioned in the literature in 1967.³³⁰ This triazide was synthesized (yield >95%) from appropriate cyanuric trichloride and sodium azide in refluxing acetonitrile. In 2012, Becker *et al.*³³¹ developed an efficient route to triazide **590** starting from mesitylene (**591**), wherein tribromide **592** was reacted with sodium azide in the final step upon heating in acetonitrile (Scheme 174).

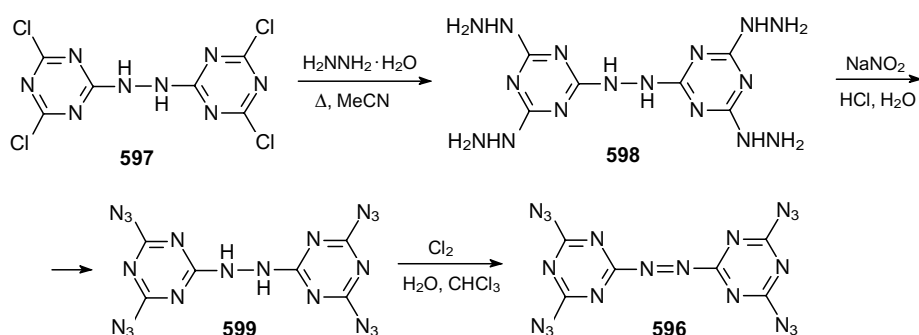
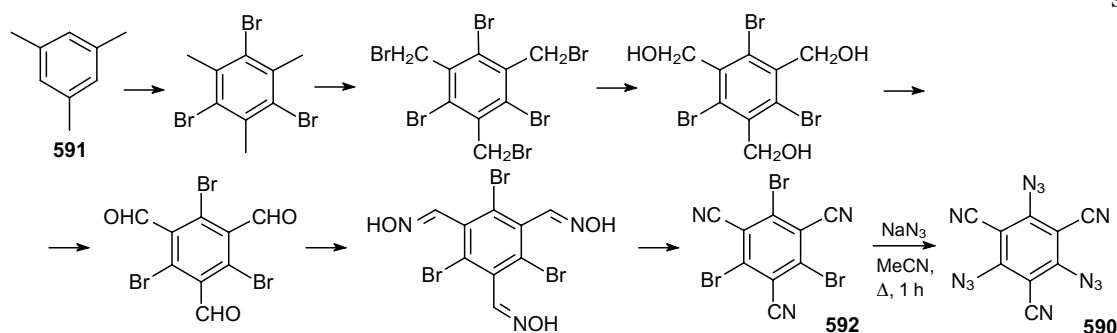
The preparation of 2,4,6-triazido-3,5-dichloropyridine (**573**) from tetrachloride **593** as well as some chemical transformation of this product were described by Ranjbar-Karimi *et al.*³³² (Scheme 175). Also noteworthy is the possibility of the selective reaction of triazide **573** with norbornene at the 4-positioned azido moiety to give aziridine **594**. In contrast, the reaction with dimethyl acetylene-



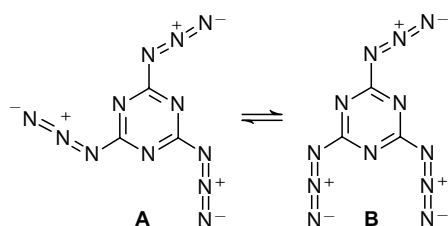
dicarboxylate produces cycloadduct **595**, the formation of which involves 2- and 6-positioned azide moieties.

Cyanuric triazide (**557**) was first reported more than 90 years ago¹³⁰ It is difficult to judge whether the compound the author dealt with was individual in view of the imperfect analytical base. After a long time, this triazide and relevant tetraazide **596** were mentioned in publications^{333,334} in 2004, devoted to studies of various polyazido high-nitrogen compounds. Scheme 176 shows the reaction sequence, as a result of which the chlorine atoms in tetrachloride **597** were first replaced with hydrazide moieties (intermediate **598**) and then by azide ones. In the final step, hydrazide derivative **599** was converted to the corresponding aza compound **596**.

In 2004, Zheng *et al.*³³⁵ performed quantum chemical calculations of compounds **557**, **596** and other heterocyclic polyazides and also predicted the azide–tetrazole tautomerism. The energy difference between the conformations A



Scheme 177



and **B** of triazide **557** is as low as 0.3 kcal mol⁻¹, while the energy of the transition state is 11.7 kcal mol⁻¹ (Scheme 177).³³⁶

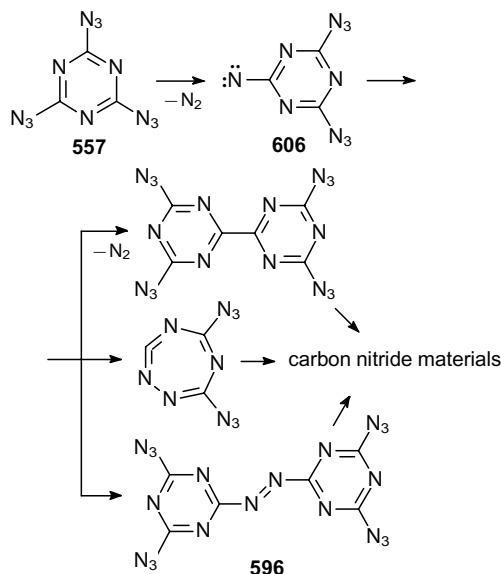
The azide–tetrazole ring-chain tautomerism was studied for a wide range of aromatic di-, tri- and tetraazides **557**, **596**, **599**–**605** (Scheme 178).³³⁷ *Ab initio* quantum-chemical methods showed that the electron-donating amino group promotes the ring closure of tetrazoles, while the electron-withdrawing nitro group favours the retention of the azido form. It was predicted that diazidoazo- and hydrazotetrazines would readily cyclize to tetrazoles in polar solvents.³³⁸

An unambiguous assignment of signals in the ¹⁵N NMR spectra of 2,4,6-triazido-*s*-triazine, 2,4,6-triazidopyrimidine and six 2,4,6-triazidopyridines was made using computational and experimental methods. The different reactivity of α - and γ -azido moieties of pyridines correlates well with the ¹⁵N chemical shifts in the NMR spectra. Among two non-equivalent azido functionalities of azines, an azido moiety with a more downfield shifted ¹⁵N signal is more electron-deficient and reactive towards electron-rich agents. In contrast, an azido moiety with the most upfield shifted ¹⁵N signal is the most reactive towards electron-poor reagents.³³⁹

In 2000, it was shown³⁴⁰ that the slow thermal decomposition of compound **557** in a high-pressure reactor produces nitrogen-rich carbon nitrides (Scheme 179). The authors suggested that in this case, the elimination of one nitrogen molecule affords intermediate **606** followed by its transformations.

The resulting material is an amorphous bulk solid having a glassy microstructure with large pores and voids. Compound **557** can be used to prepare amorphous films exhibiting optical properties. This triazide can be employed to deposit carbon nitride coatings onto a wide range of thermally sensitive substrates.³⁴¹ The recent advances in this field are discussed in a review³⁴² published in 2021.

Scheme 179

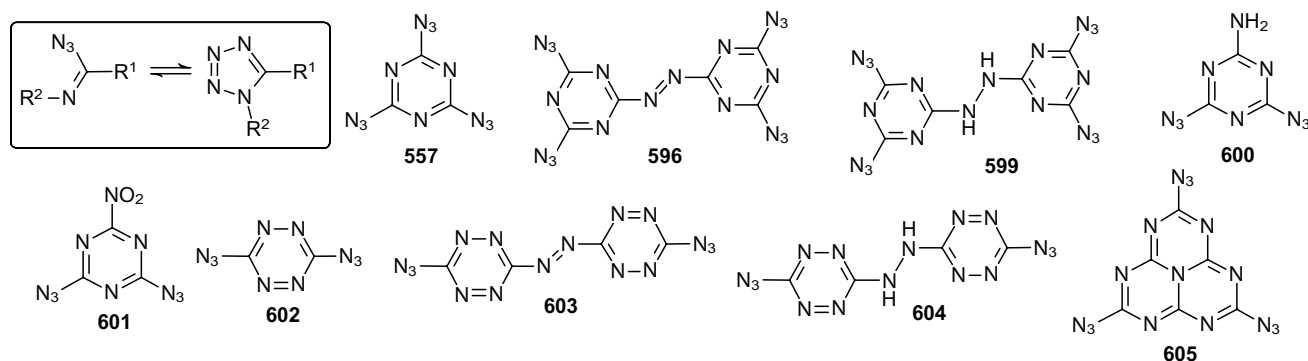


4.4. High-molecular-weight polyazides

Polyazides are being extensively studied as coupling agents for the construction of nitrogen-containing macromolecules. Highly branched structures, such as dendritic and star-shaped polymers, have been of great interest to researchers for a long time due to their compact structure and high functionality of the end groups. This is the subject of a review by Lammens and Du Prez.³⁴³ The synthesis of high-molecular-weight polymers involving di- and polyazides is generally based on a convenient azide–alkyne [3 + 2]-cycloaddition reaction. It provides controlled cross-linking of shorter chains, resulting in nodal nets of 1,2,3-triazoles.³⁴⁴ The CuAAC reaction is commonly used to design materials with architectural integrity due to the presence of stable triazole moieties in their structure. The reported examples include linear polymers, dendrimers, polymer networks, polymer nanoparticles and other high-molecular-weight structures.³⁴⁵

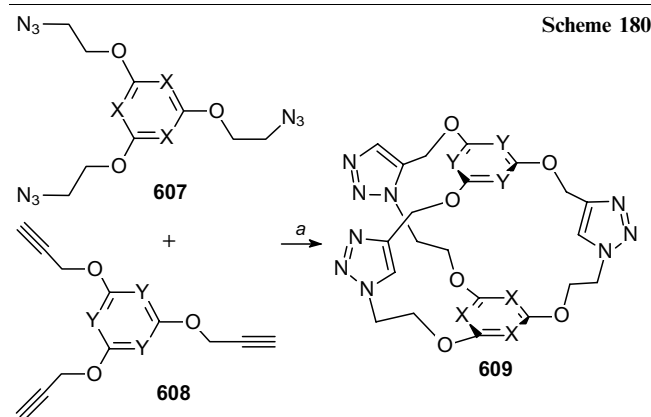
Brunner *et al.*³⁴⁶ developed dendritic siRNA nanostructures capable of penetrating even difficult-to-transfect cells such as neurons due to a special receptor ligand. The cell-penetrating siRNA dendrimers, constructed using click chemistry methodology, provide great opportunities for finding novel molecules that are able to treat, *e.g.*, fatal illness caused by the rabies virus.

Scheme 178



1,2,3-Triazole cross-linked polymers were synthesized as binders for solid rocket propellant systems by reacting the azide moieties of the polymer with the alkyne groups of a dipolarophile curing agents. A carbonyl functionality adjacent to the triple bond, which acts as an electron-withdrawing group, significantly accelerates the 1,3-dipolar cycloaddition reaction between azide and alkyne functionalities, allowing the preparation of rubbery materials with a high degree of cross-linking.³⁴⁷

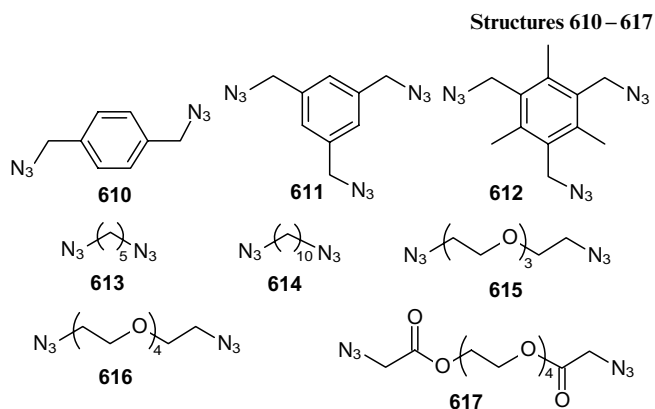
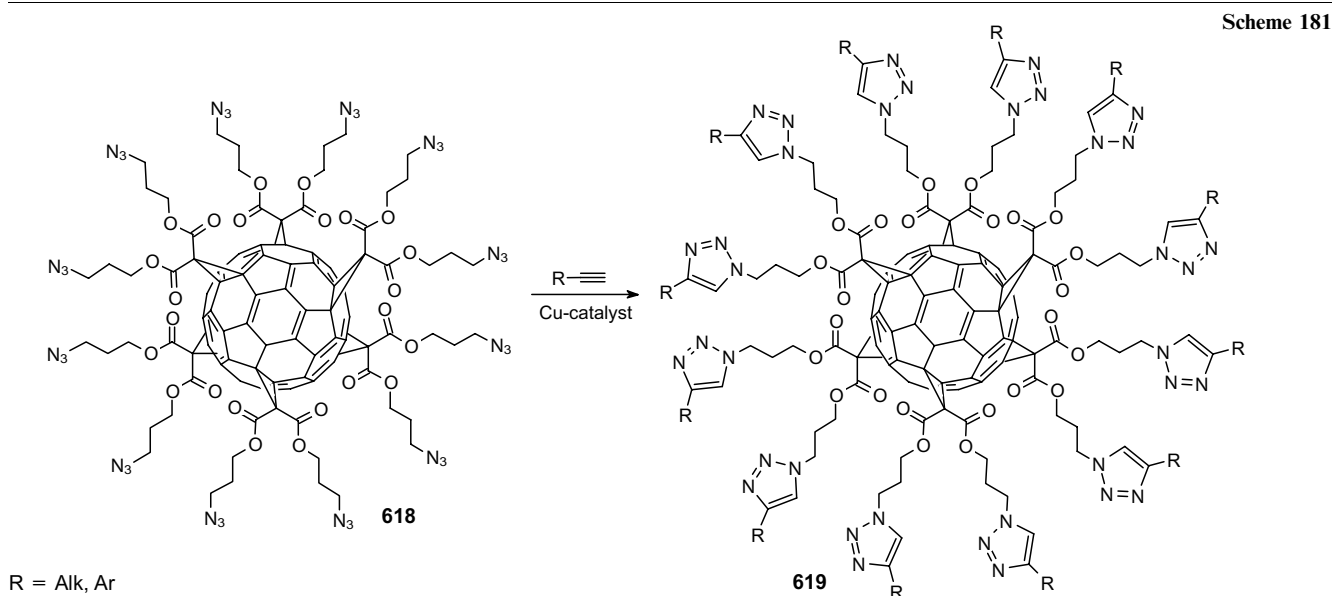
The covalent synthesis of nanoscale frameworks is easily carried out in high yields using click chemistry methodology via the Cu^I-catalyzed cycloaddition of appropriate polyazides **607** and polyalkynes **608** in the presence of (EtO)₃P·CuI as the catalyst to afford structures **609** (Scheme 180).³⁴⁸



(a) (EtO)₃P·CuI, DIPEA, PhMe, MW; X = Y = N (78%);
X = N, Y = CH (92%); X = Y = CH (95%);
DIPEA is diisopropylethylamine

A similar approach was implemented to produce cured polymers based on commercial polyols.³⁴⁹ Compounds **610–617** were used as an azide component.

The click chemistry concept was employed to construct fullerene building blocks based on azide-containing fullerenes. Scheme 181 illustrates one such example, the conversion of polyazide **618** into polytriazole **619**. Current investigations in this field are summarized in a review.³⁵⁰



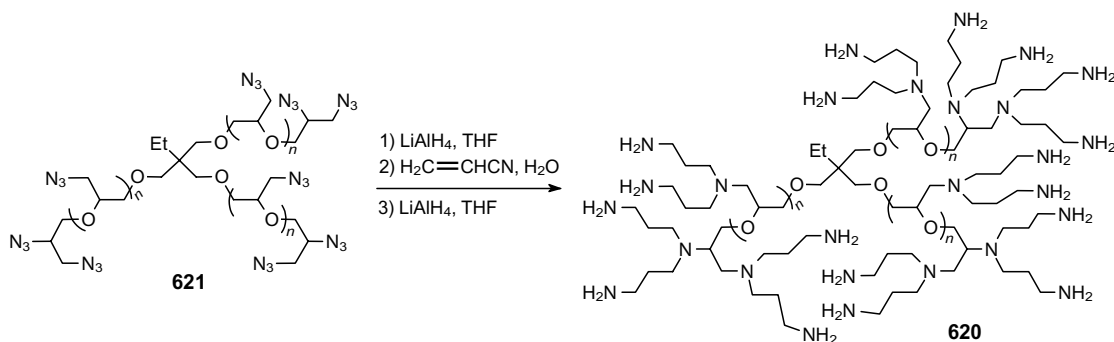
Hiba and Sreekumar³⁵¹ presented the synthesis of dendrimer **620** from appropriate polyazide **621** (Scheme 182). In the resulting product, the dendritic cavity and surface are functionalized with reactive centres. This amino-functionalized dendronized polymer was used as a homogeneous organocatalyst for the synthesis of 4-substituted triazoles.

Conventional thermosetting polyurethane polymers are prepared by crosslinking a polyisocyanate with a polyol. An alternative approach to cross-linked polymers is possible using polyazides. Figure 1 shows a general strategy for obtaining novel promising polymer materials based on azide-containing polymers.^{352, 353}

The azide–alkyne cycloaddition allows the creation of novel structural motifs in DNA nanotechnologies and the introduction of new functional groups into DNA nanostructures,³⁵⁴ and also have proved to be effective in the synthesis of fluorinated surfactants for droplet microfluidics.³⁵⁵

5. Conclusion

To summarize, the chemistry of 1,1- and 1,2-diazides has attracted great interest of experts and has been extensively developed in recent years. Noteworthy is the importance of these classes of azides in modern organic chemistry. This review presents a large number of various methods for the



synthesis of such compounds, including stoichiometric, catalytic, photochemical and even electrochemical approaches. It is important to highlight high reactivity of diazides and a variety of their reactions, from thermal transformations to click reactions. Of particular attention are processes, in which one azide functionalities undergoes intramolecular cyclization, while another azide moiety remains intact. This enables further chemical transformations involving the remaining azido moiety of the resulting heterocycles, in particular of azidoisoxazoles and azido-1,2,3-triazoles. Tri- and tetraazides are often investigated as precursors to explosives and monomers in macromolecular chemistry. In general, this line of research has so far been studied only fragmentary and there is a wide field of activity for organic chemists and researchers in related disciplines.

* * *

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6. List of abbreviations and designations

The following abbreviations and designations are used in the review:

- Boc — *tert*-butoxycarbonyl;
- BHT — 2,6-di-*tert*-butyl-4-methylphenol;
- Bs — benzenesulfonyl;
- CuAAC — click reaction of copper-catalyzed azide-alkyne cycloaddition;
- DABCO — 1,4-diazabicyclo[2.2.2]octane;
- DCE — 1,2-dichloroethane;
- DCM — dichloromethane;
- DEA — diethylamine;
- DEAD — diethyl diazodicarboxylate;
- DFT — density functional theory;
- DIPEA — diisopropylethylamine;
- DMAP — 4-dimethylaminopyridine;
- DNABT — 1,1'-dinitramino-5,5-bis(tetrazole);
- dr* — diastereomeric ratio;
- Fmoc — 9-fluorenylmethoxycarbonyl;
- IBX — 2-iodoxybenzoic acid;

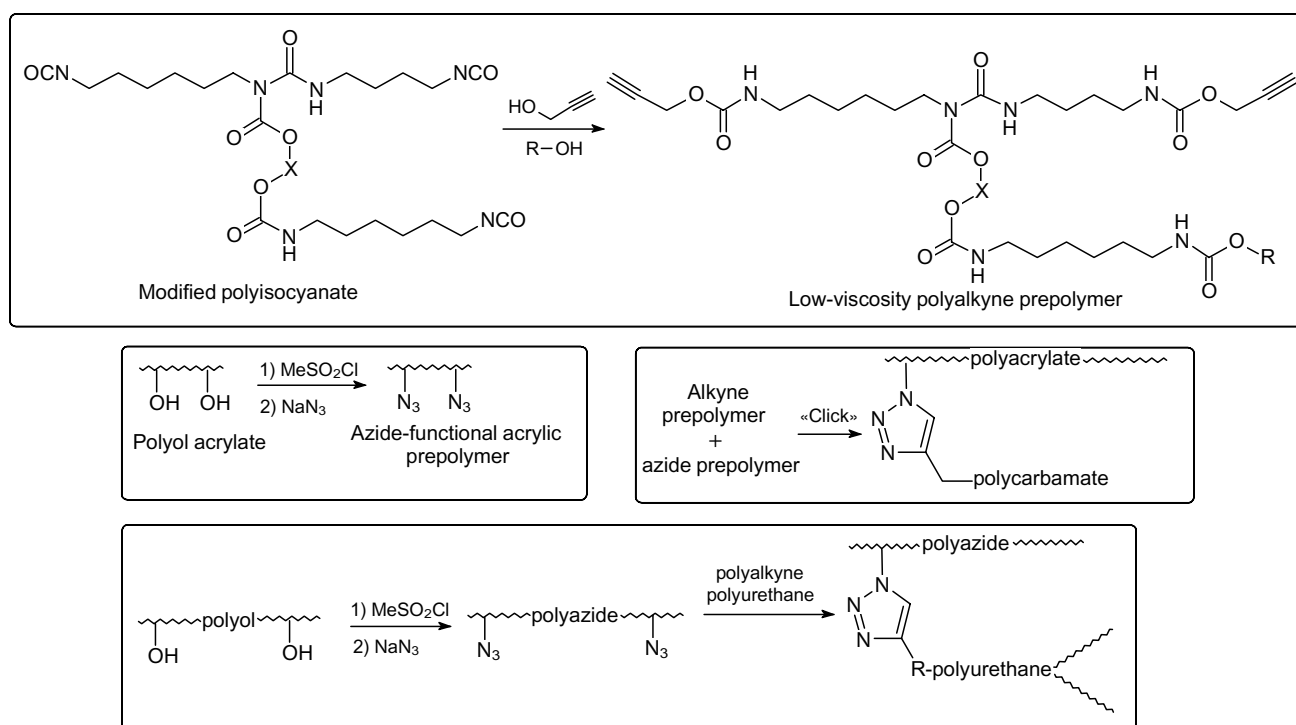


Figure 1. General strategy for obtaining polymer materials based on azide-containing polymers.

IBX-SO₃K — potassium 3-carboxy-4-iodylbenzenesulfonate;

KHMDS — potassium bis(trimethylsilyl)amide (potassium hexamethyldisilazide);

L — ligand;

LDA — lithium diisopropylamide;

MOM — methoxymethyl;

Ms — methanesulfonyl (mesyl);

MW — microwave irradiation;

NBS — *N*-bromosuccinimide;

NFSI — *N*-fluorobenzenesulfonimide;

NIS — *N*-iodosuccinimide;

PMB — *p*-methoxybenzyl;

PIFA — bis(trifluoroacetoxy)iodobenzene;

Py — pyridyl;

4-PPY — 4-pyrrolidinopyridine;

SET — single electron transfer;

SPAAC — strain-promoted azide–alkyne cycloaddition;

TBAB — tetra-*n*-butylammonium bromide;

TBAF — tetra-*n*-butylammonium fluoride;

TBPB — *tert*-butyl peroxybenzoate;

TBS — *tert*-butyldimethylsilyl;

TEMPO — (2,2,6,6-tetramethylpiperidin-1-yl)oxyl;

TFA — trifluoroacetic acid;

Tf — trifluoromethanesulfonyl (triflyl);

Th — thienyl;

TIPS — triisopropylsilyl;

TMGA — tetramethylguanidinium azide;

TMS — trimethylsilyl;

Troc — 2,2,2-trichloroethoxycarbonyl;

Ts — *p*-toluenesulfonyl (tosyl).

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