

RECENT PROGRESS IN THE CHEMISTRY OF POLYAZIDOAZINES

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Abstract. *Di-, tri- and tetraazido-substituted azines are of considerable interest as high-energy organic materials and precursors of carbon nitride nanomaterials as well as photoactive cross-linking agents in polymer chemistry and molecular biology, photoresists in microelectronics and as starting compounds in organic synthesis and photochemistry. This review is devoted to the recent progress in the synthesis and chemical transformations of various azines bearing several azido groups in the azine ring.*

Contents

1. Introduction
 2. High-energy polyazidoazines
 3. Heterocyclic nanostructures from polyazidoazines
 4. Reactivity of polyazidoazines
 5. Organic molecular magnets from polyazidoazines
 6. Conclusion
- Acknowledgement
References

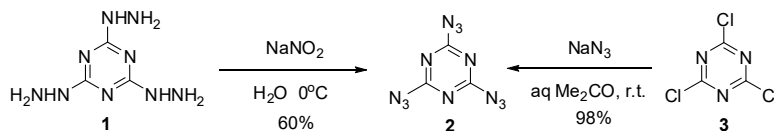
1. Introduction

On comparison with di- and triamination reactions, the polyazidation of halogenated azines takes place under remarkably mild conditions, often at room temperature, providing access to various polyfunctionally-substituted azines.^{1,2} The products of these azidation reactions are di-, tri- and tetraazidoazines, the azido groups of which can selectively react with dipolarophiles, reductants, phosphines, and phosphites or undergo selective photolysis and thermolysis to form diverse new heterocyclic compounds.³⁻⁶ Moreover, many of di-, tri- and tetraazidoazines are themselves of considerable practical interest and widely used as ecologically friendly primary explosives⁷ and high-energy materials,⁸⁻³⁷ anti-cancer drugs,³⁸ precursors of carbon nitride nanomaterials and nanotubes,^{13,39-45} photoresists in microelectronics¹ and as photoactive cross-linking reagents in polymer chemistry and molecular biology.^{1,46} This review is devoted to the recent progress in the synthesis and chemical transformations of azines bearing several azido groups in the azine ring.

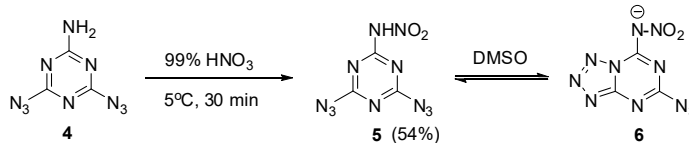
2. High-energy polyazidoazines

The azido group is one of the most energetic functional groups, adding about 290 kJ/mol to the energy content of a molecule.¹¹ On the other hand, azines themselves possess inherent positive heat of formation. Therefore, the synthesis of di-, tri- and tetraazido-substituted azines is of considerable interest in the chemistry of high-energy organic materials. The first representative of this class of energetic compounds, 2,4,6-triazido-*s*-triazine **2**, has been obtained by diazotization of 2,4,6-trihydrazino-*s*-triazine **1** in 1907 (Scheme 1).⁴⁷ Nowadays, this triazide is readily prepared in almost quantitative yield by slow addition of solid sodium azide to a solution of cyanuryl chloride **3** in acetone at room temperature (Scheme 1).⁴⁸ Although the preparation of triazide **2** is very simple, all necessary precautions (Kevlar gloves, wrist protectors, face shield, ear protection, and thick leather coat) should be applied in the work since very high sensitivity of this triazide toward impact, friction and electrostatic discharge.⁷ Moreover, triazide **2** is very volatile and starts to sublime already at moderate temperatures (>40 °C).²⁶ To obtain more thermally stable and less sensitive high-energy polyazides, various derivatives of triazide **2** such as diazide **5**,^{17,18} triazide **8**,¹² tetraazides **10**,⁸ **11**⁹ and **13**³¹ as well as diazide **15** have been synthesized in the last years (Schemes 2-5). Among all these compounds, diazide **15** has the highest positive heat of formation $\Delta H_f = 1101$ kJ/mol (6709 kJ/kg) and is the most sensitive toward impact, friction and electrostatic discharge.^{10,11} This diazide is readily obtained by diazotization of 3,6-dihydrazino-*s*-triazine **14** and undergoes the azide-tetrazole tautomerization in DMSO solutions to form azidoterazole **16** (Scheme 5).¹¹ Recently, new high-energy tetraazidoazines **18**

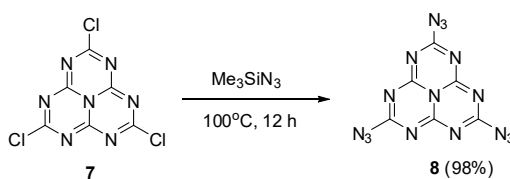
and **19** have been obtained, the molecules of which were built from energetic *s*-triazine and 1,2,4,5-tetrazine rings (Scheme 5).³⁷ On comparison with diazide **15**, tetraazides **18** and **19** are much more thermally stable and less sensitive to impact and friction.



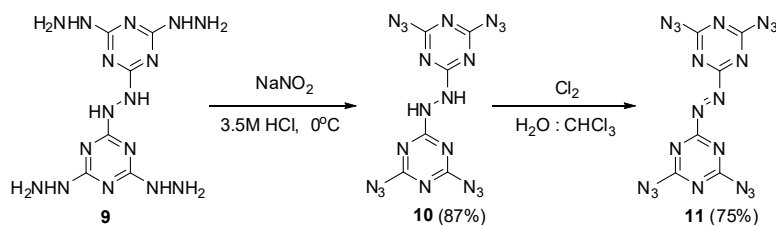
Scheme 1. Methods of preparation of triazide **2**.



Scheme 2. Synthesis and tautomerization of diazide **5**.



Scheme 3. Synthesis of triazide **8**.

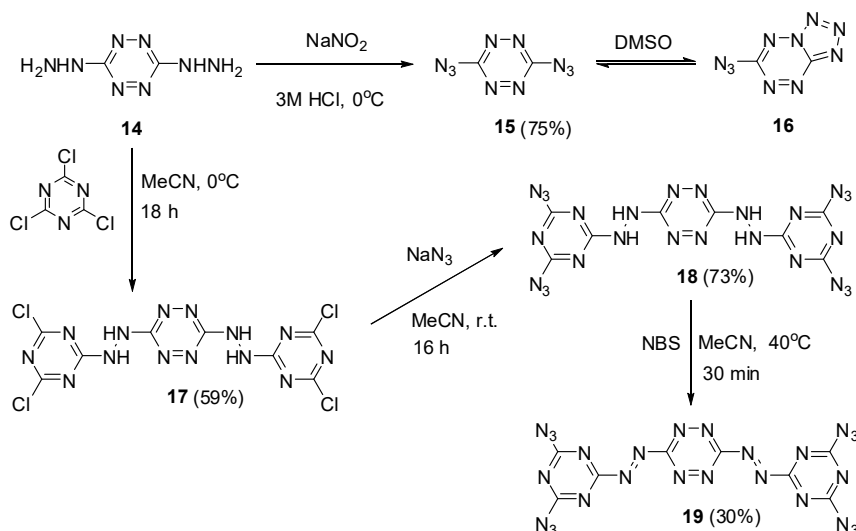


Scheme 4. Synthesis of high-energy tetraazides **10**, **11** and **13**.

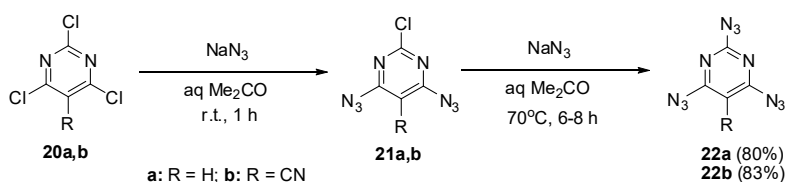
On comparison with azido-*s*-triazines and azido-1,2,4,5-tetrazines, azidopyrimidines are much less sensitive to impact and friction, preserving at the same time useful energetic characteristics. Two high-energy triazidopyrimidines **22a**³² and **22b**³³ are readily obtained in high yields by boiling of the corresponding chlorides **20a,b** with sodium azide in aqueous acetone (Scheme 6). At room temperature, these reactions are completed at the stage of formation of diazides **21a,b**.³³

To achieve very high positive heats of formation for molecules of azidopyrimidines, the methods of preparation of tetraazide **25** and pentaazide **29** have been developed.¹³ The bromination of methylpyrimidine **23** with *N*-bromosuccinimide (NBS) gave compound **24** in high yield (Schemes 7). The latter readily underwent tetraazidation to form compound **25** in almost quantitative yield. The reaction of barbituric acid **26** with DMF and POCl₃ gave trichloro-substituted aldehyde **27** that underwent triazidation to form triazide

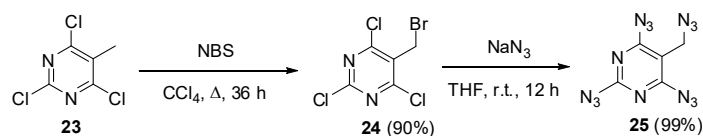
28 (Schemes 8). This triazide, without isolation, was used in the reaction with tin dichloride and trimethylsilylazide (TMSA), yielding pentaazide **29** in moderate yield.



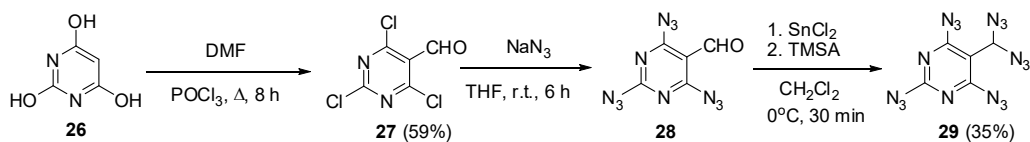
Scheme 5. Methods of preparation of high-energy diazide **15** and tetraazides **18** and **19**.



Scheme 6. Synthesis of high-energy triazides **22a,b**.



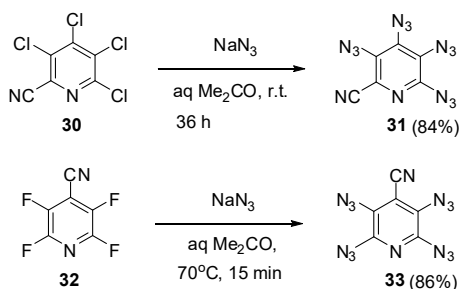
Scheme 7. Synthesis of high-energy tetraazide **25**.



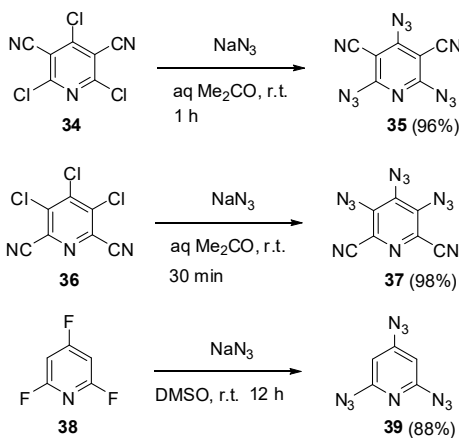
Scheme 8. Synthesis of high-energy pentaazide **29**.

On comparison with pyrimidine, pyridine has smaller positive heat of formation. On the other hand, the presence of five carbon atoms in the pyridine ring allows the introduction of five energetic groups, for instance, the azido (+290 kJ/mol) and cyano (+120 kJ/mol) groups.¹⁴ Thus, it was found that azidation of tetrachloropyridine-2-carbonitrile **30** and tetrafluoropyridine-4-carbonitrile **32** with sodium azide in acetone affords tetraazides **31**¹⁴ and **33**³⁰ possessing the very high positive heats of formation (Scheme 9). Some of azidoazines such as triazides **35**,¹⁴ **37**²⁹ and **39**⁴⁹ may be of considerable interest as energetic gasifying agents

of solid fuels for ramjet engines.³⁶ These triazides are readily obtained by triazidation of the corresponding halides **34**, **36** and **38** in appropriate solvents at room temperature (Scheme 10).

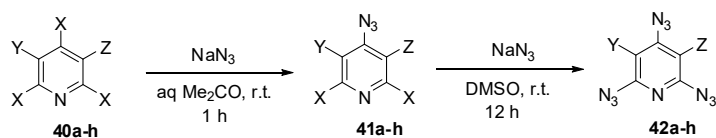


Scheme 9. Synthesis of high-energy tetraazides **31** and **33**.



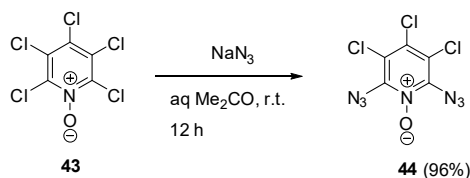
Scheme 10. Synthesis of triazides **35**, **37** and **39**.

It should be noted that facile substitutions of halogens for the azido groups in pyridines takes place only when the pyridine ring is activated by strong electron-withdrawing groups as in the case of compounds **30**, **32**, **34** and **36** (Schemes 9 and 10). By analogy with these pyridines, activated halopyridines **40a-c** also readily react with excess sodium azide in acetone at room temperature to afford triazides **42a-c** in 90-96% yields (Scheme 11).^{50,51} However, the reactions of non-activated halopyridines **40d-h** with excess sodium azide in acetone at room temperature yield, as a rule, only monoazide **41d-h**.^{49,52-54} The *tris*-azidation of halopyridines **40d-h** at room temperature efficiently proceeds in DMSO to give triazidopyridines **42d-h** in 94-98% yields (Scheme 11).^{49,52-54} It is also interesting to note that very strongly activated *N*-oxide **43** does not undergo the *tris*-azidation even on boiling in DMSO to form only diazide **44** (Scheme 12).⁵⁵



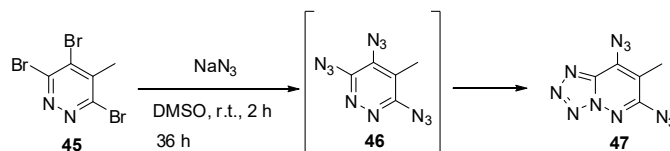
a: X = Y = Cl, Z = CN; **b:** X = Y = Cl, Z = CF₃; **c:** X = Y = F, Z = CN; **d:** X = Y = F, Z = Cl;
e: X = Y = Z = F; **f:** X = Y = Z = Cl; **g:** X = Y = Z = Br; **h:** X = Y = Z = I

Scheme 11. Synthesis of triazides **42a-h**.



Scheme 12. Azidation of pentachloropyridine-*N*-oxide **43**.

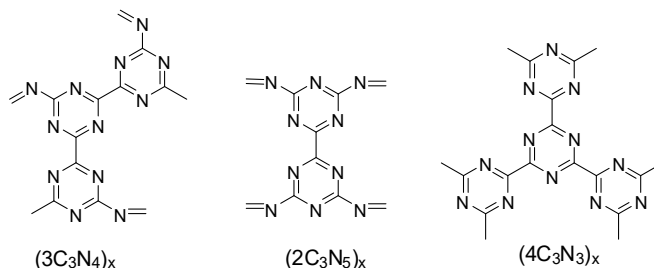
So far, almost nothing is known about the synthesis and properties of polyazidopyrazines and polyazidopyridazines that may be of considerable interest as energetic organic materials. It was only reported that azidation of tribromide **45** with sodium azide in DMSO at room temperature affords diazidotetrazole **47** in 45% yield via intermediate formation of triazide **46** (Scheme 13).⁵⁶



Scheme 13. Azidation of tribromide **45**.

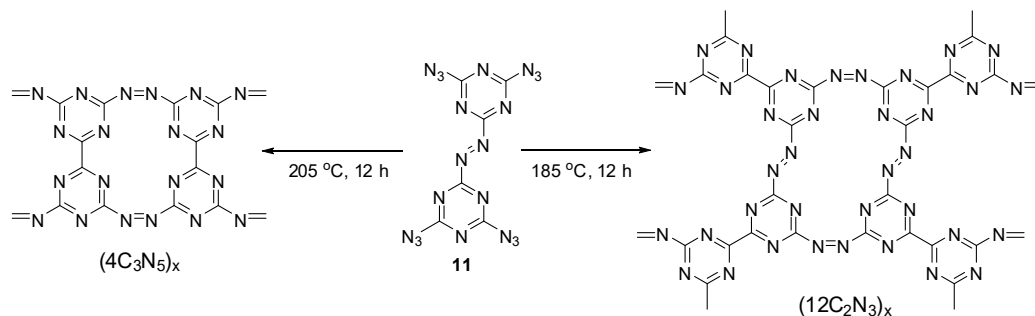
2. Heterocyclic nanostructures from polyazidoazines

Thermolysis of polyazidoazines allows the preparation of various carbon nitride (CN_x) nanomaterials, *e.g.* nanotubes, nanoclusters, nanodendritic and nanolayered carbon nitrides.^{10,13,43} These materials possess unique mechanical, chemical, optical and tribological properties including low density, surface roughness, wear resistance, chemical inertness and biocompatibility. Triazide **2** was the first representative of polyazidoazines used for design of carbon nitride (CN_x) nanomaterials. The slow thermolysis of this triazide at 185 °C and 1 atm of N₂ for 2 days led to the formation C₃N₄ carbon nitride in the form of orange-brown powder.⁴⁰ However, when the above decomposition was performed in a reactor pressurized with 6 atm of N₂, the product consisted of brown, hard, brittle millimeter-sized pieces with a C₃N₅ formulation was obtained. Both products transformed into black C₃N₃ carbon nitride on heating at 650 °C. Possible elementary units of these three products are depicted in Scheme 14.



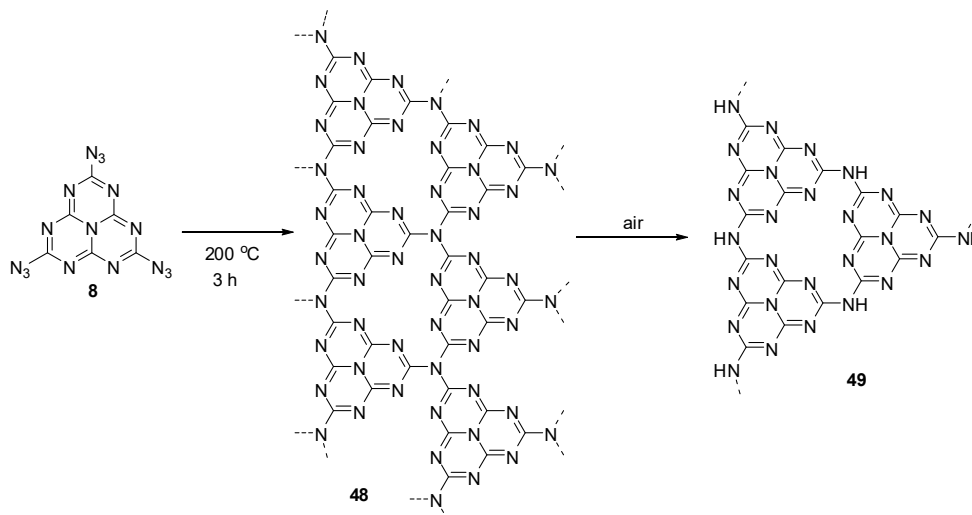
Scheme 14. Possible elementary units in C₃N₄, C₃N₅ and C₃N₃ carbon nitrides.

The C₃N₅ carbon nitrides are also readily obtained during the thermolysis of tetraazide **11** at 205 °C and ambient pressure for 12 h. On the other hand, slow thermal decomposition of the same tetraazide at 185 °C for 12 h produced a new type of carbon nitrides with a C₂N₃ formulation.⁴³ Possible elementary unit of this product is depicted in Scheme 15.



Scheme 15. Thermal transformations of tetraazide **11**.

The thermal decomposition of triazide **8** at various temperatures also leads to the formations of $(CN)_x$, where $x > 1.3$ carbon nitrides.⁴⁴ Thus, the thermolysis of this triazide at 185 °C under argon atmosphere for 3 h yields carbon nitride **48** (Scheme 16). The latter undergoes hydrogenation on air to form product **49**.



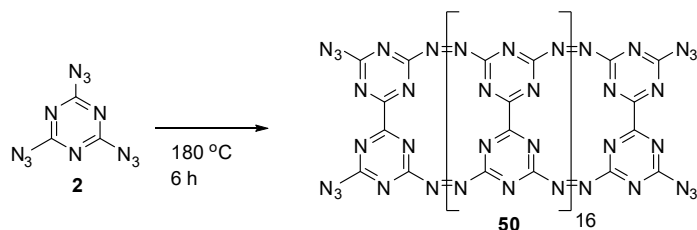
Scheme 16. Thermal transformations of triazide **8**.

On comparison with traditional synthetic methods, thermal decomposition of azidoazines provides relatively simple approach to preparation of a great variety of new nitrogen-rich heterocyclic systems. For example, the use of short times and moderate temperatures during thermolysis of polyazidoazines allows the preparation of new polyazides possessing extended nitrogen-rich heterocyclic system. Thus, the thermolysis of triazide **2** at 185 °C under argon atmosphere for 6 h yields tetraazide **50** (Scheme 17).⁴⁵ In the case of thermolysis of triazide **39** at 160 °C under argon atmosphere for 6 h, the product of the reaction is diazide **51** (Scheme 18).⁴⁵ Similar diazide **52** along with tetraazide **53** are formed in the thermolysis of triazide **22a** at 160 °C under argon atmosphere for 6 h (Scheme 19).⁴⁵

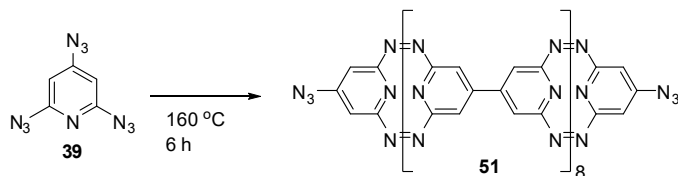
4. Reactivity of polyazidoazines

All polyazidoazines are electron deficient compounds and readily react with electron-rich reagents, *e.g.* reductants, amines, phosphines, phosphites and electron-rich dipolarophiles.^{3,4} Thus, the reaction of triazide **35** with an equimolar amount of tin dichloride occurs selectively on the most electron deficient azido group in the γ -position of pyridine ring to give amine **54** as a sole product (Scheme 20).⁵⁷ By using excess of

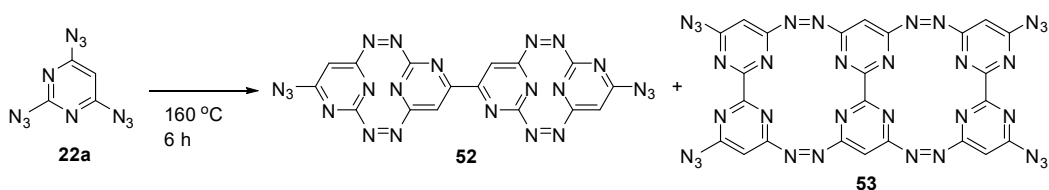
SnCl_2 , diazide **54** undergoes further reduction to form diamine **55**. The less electron deficient triazide **42f** is reduced with an excess of SnCl_2 under similar conditions only till monoamine **56** (Scheme 20).⁵⁷



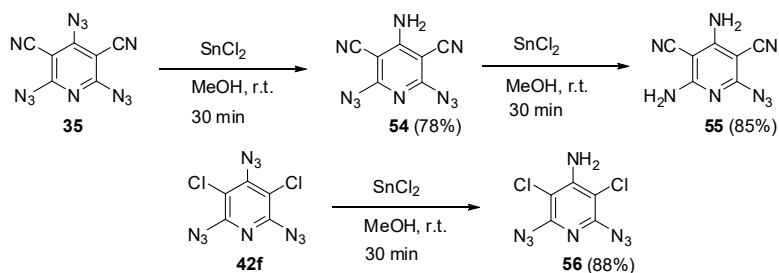
Scheme 17. Incomplete thermolysis of triazide **2**.



Scheme 18. Incomplete thermolysis of triazide **39**.



Scheme 19. Incomplete thermolysis of triazide **22a**.



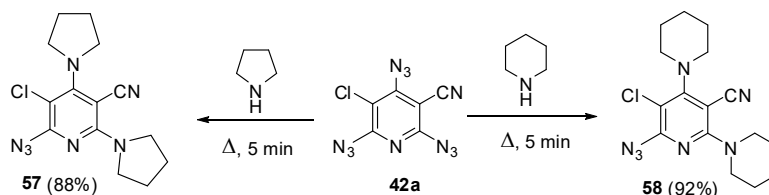
Scheme 20. Reduction of triazides **35** and **42f**.

Triazide **42a** readily reacts with pure pyrrolidine and piperidine to form diamines **57** and **58** (Scheme 21).⁵⁸ When amination of polyazidoazines is carried out in water solutions, only monoaminated products are formed. Thus, the reactions of triazide **2** with amines $\text{R}^1\text{R}^2\text{NH}$ afford aminodiazides **59a-n** in 65-85% yields (Scheme 22).⁶

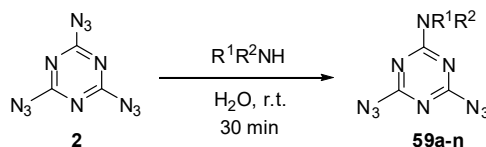
The Staudinger reactions of triazides **35** and **42a,f** with triphenylphosphine in ether at $0\text{ }^\circ\text{C}$ also occurs selectively on the most electron-deficient γ -azido groups to give iminophosphoranes **60a-c** in 93-97% yields (Scheme 23).⁵⁹ In turn, diazide **60b** reacts with an excess of triphenylphosphine on boiling in benzene to give *tris*-adduct **61** in 80% yield.⁵⁰

On comparison with triphenylphosphine, triethylphosphite is less reactive toward azides. The reaction of triazide **42g** with equimolar amount of triethylphosphite in ether efficiently proceeds only at room

temperature to give *mono*-adduct **62** as a sole product (Scheme 24).⁵⁴ Two equivalents of triethylphosphite readily react with triazide **42g** on boiling in benzene for 2 h to give the mixture of azide **63** and tetrazole **64**. The treatment of this mixture of compounds with 5% HCl gives azide **65** as a sole product. The reaction of triazide **41f** with three equivalents of triethylphosphite on boiling in benzene for 12 h yields *tris*-adduct **66**.

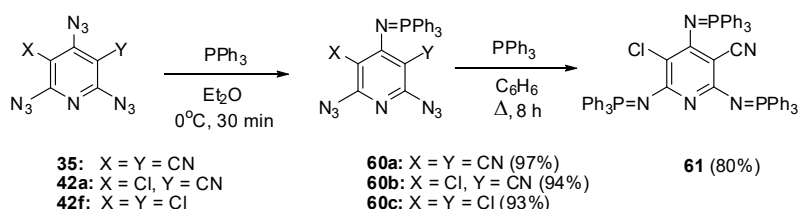


Scheme 21. Amination of triazide **42a** with pyrrolidine and piperidine.



R^1R^2N- = **a**: MeHN-; **b**: EtHN-; **c**: Me₂N-; **d**: PrHN-; **e**: *t*-PrHN-; **f**: BuHN-; **g**: *t*-BuHN-;
h: *t*-BuHN-; **i**: CH₂:CHCH₂HN-; **j**: *n*-HexHN-; **k**: MeOCH₂CH₂HN-;
l: MeO(CH₂)₃HN-; **m**: cyclohexylamino; **n**: morpholino

Scheme 22. Amination of triazide **2** in water solutions.

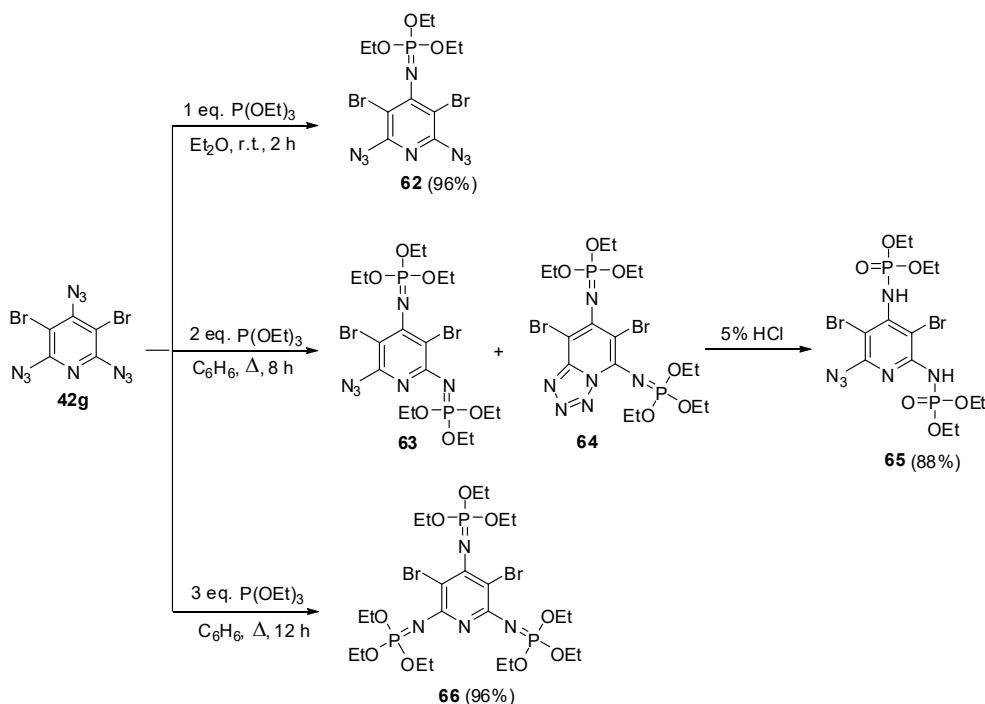


Scheme 23. Reactions of triazides **35** and **42a,f** with triphenylphosphine.

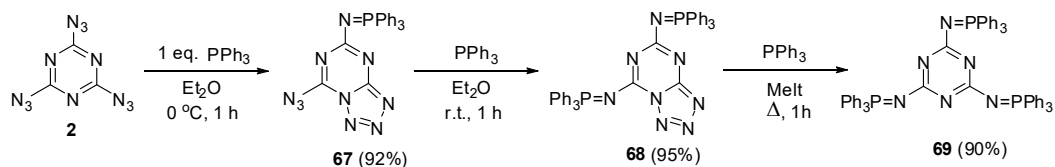
The Staudinger reaction of triazide **2** with equimolar amount of triphenylphosphine in ether at 0 °C leads to *mono*-adduct **67** that may react with an excess of triphenylphosphine in ether at room temperature to form *bis*-adduct **68** (Scheme 25).⁶⁰ The latter does not react with triphenylphosphine in solutions even at elevated temperatures. However, the melting of compound **68** with an excess of triphenylphosphine affords *tris*-adduct **69** in high yield.

Triazides **35** and **42a,f** readily react with norbornene in ether at 0 °C to form *mono*-adducts **70a-c** in high yields (Scheme 26).^{61,62} In turn, electron-deficient diazide **70a** reacts with an excess of norbornene at room temperature, yielding *tris*-adduct **71a**. Similar *tris*-adducts **71b** and **71c** can be obtained in good yields either by boiling of azides **70b** and **70c** with an excess of norbornene in benzene or in reactions of the same diazides with an excess of norbornene in ether at room temperature in the presence of dirhodium tetraacetate as a catalyst.

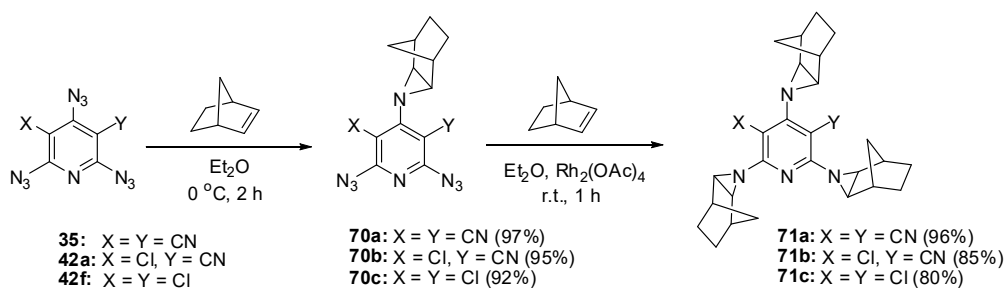
In ether at 0 °C, extremely reactive *tert*-butylphosphaacetylene selectively reacts with the γ -azido group of triazide **35** to give *mono*-adduct **72a** in 75% yield (Scheme 27).^{63,64} The latter reacts with an excess of *tert*-butylphosphaacetylene in ether at 0 °C to form *tris*-adduct **73a** in 80% yield. By contrast, the reaction of triazide **42a** with one molar equivalent of *tert*-butylphosphaacetylene in ether at 0 °C affords the mixture of *mono*-adduct **72b** and *tris*-adduct **73b**. The further addition of *tert*-butylphosphaacetylene to this mixture of compounds in ether at 0 °C gives *tris*-adduct **73b** as a sole product in 80% yield.



Scheme 24. Reactions of triazide **42g** with triethylphosphite.

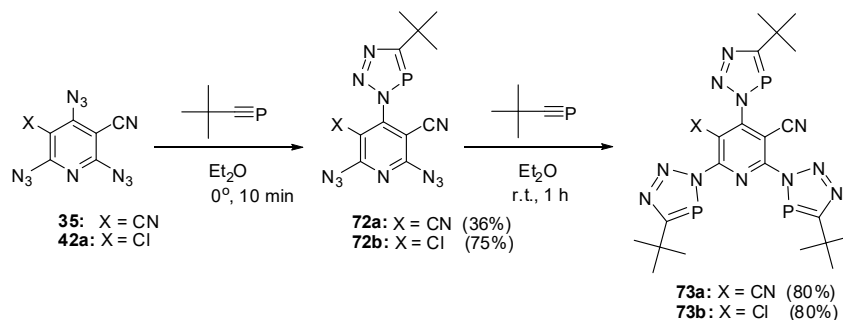


Scheme 25. Reactions of triazide **2** with triphenylphosphine.

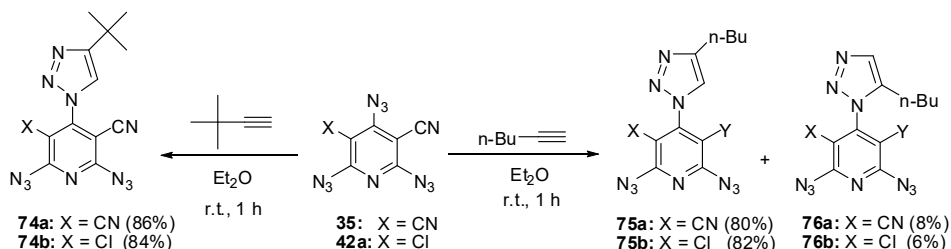


Scheme 26. Reactions of triazides **35** and **42a,f** with norbornene.

The reactions of triazides **35** and **42a** with electron-rich *tert*-butylacetylene in ether at room temperature occur regioselectively on the γ -azido groups to form *mono*-adducts **74a,b** in ~85% yield (Scheme 28).⁶⁵ Similar reactions of triazides **35** and **42a** with less sterically hindered *n*-butylacetylene give the mixtures of diazides **75a,b** and **76a,b**.⁶⁵

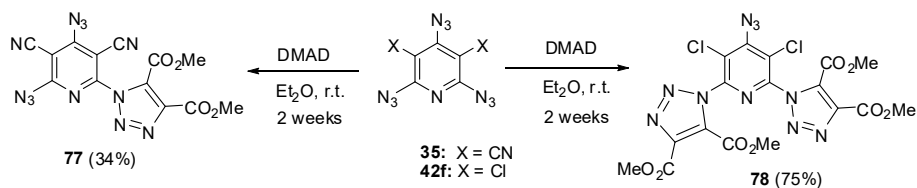


Scheme 27. Reactions of triazides **35** and **42a** with *tert*-butylphosphaacetylene.



Scheme 28. Reactions of triazides **35** and **42a** with butylacetylenes.

Since high electron-deficiency, triazides **35** and **42f** are not highly reactive toward electron-deficient dipolarophiles. The reaction of triazide **34** with an excess of dimethyl acylenedicarboxylate (DMAD) in ether at room temperature for 2 weeks occurs selectively on the least electron-deficient α -azido group to give triazole **77** in 34% yield (Scheme 29).⁶⁶ Similar reaction of less electron-deficient triazide **42f** with an excess of DMAD leads to the formation of *bis*-adduct **78** in 75% yield.⁵³



Scheme 29. Reactions of triazides **35** and **42f** with dimethyl acylenedicarboxylate.

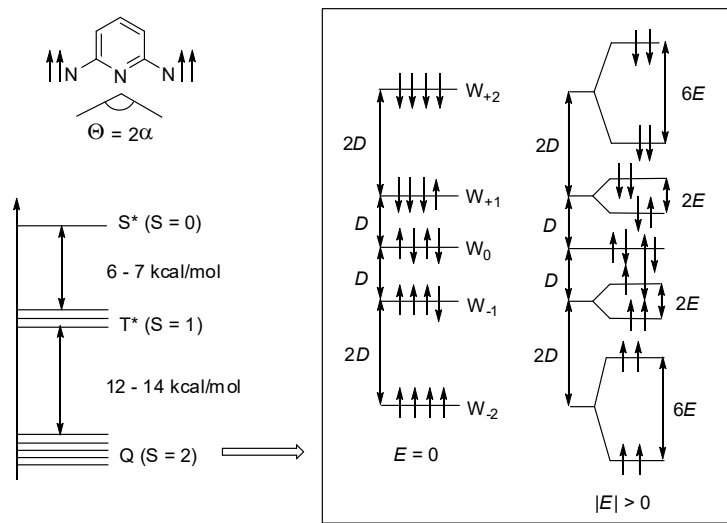
5. Organic molecular magnets from polyazidoazines

Polyazidoazines are convenient starting materials for photochemical preparation of high-spin nitrenes possessing the largest magnetic anisotropy among all organic polyradicals and representing multi-level molecular systems that may be used as qubits for quantum information processing (quantum computers).^{4,67,68} The energy splitting for molecules of quintet dinitrenes (four unpaired electrons, five-level molecular spin system, the ground quintet spin state $S=2$) and septet trinitrenes (six unpaired electrons, seven-level molecular spin system, the ground septet spin state $S=3$) is shown in Schemes 30 and 31. The energy splitting in high-spin nitrenes is described by magnetic parameters D and E that depend on spin densities ρ on the nitrene units and spatial orientation of the nitrene C–N bonds. Both these parameters, in turn, depend on the number of *endo*-nitrogen atoms and substituents in the azine ring. Thus, the variation of substituents in the azine ring allows fine tuning of magnetic properties of high-spin nitrenes, enhancing quantum coherence in molecular qubits. The D and E values of high-spin nitrenes are experimentally determined from EPR spectra. According to theory,⁶⁹ D_Q and E_Q of quintet dinitrenes depend on the triplet

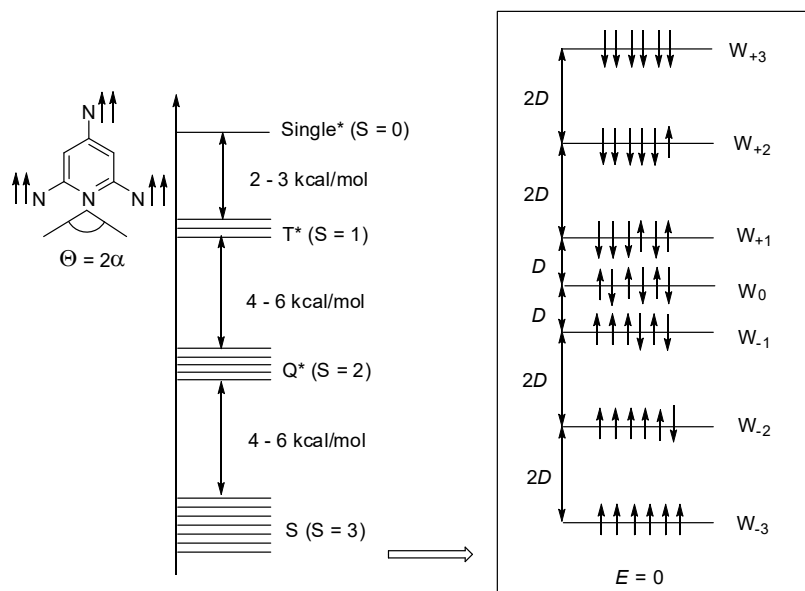
nitrene tensor D , and the dipolar angle $\Theta=2\alpha$ between the nitrene C–N bonds as shown in equations (1) and (2):

$$D_Q = D_f(2-3\cos^2\alpha)/6 \quad (1)$$

$$E_Q = D_f(\cos^2\alpha)/6 \quad (2)$$



Scheme 30. Energy splitting in five-level (S=2) quintet dinitrenes.



Scheme 31. Energy splitting in seven-level (S=3) septet trinitrenes.

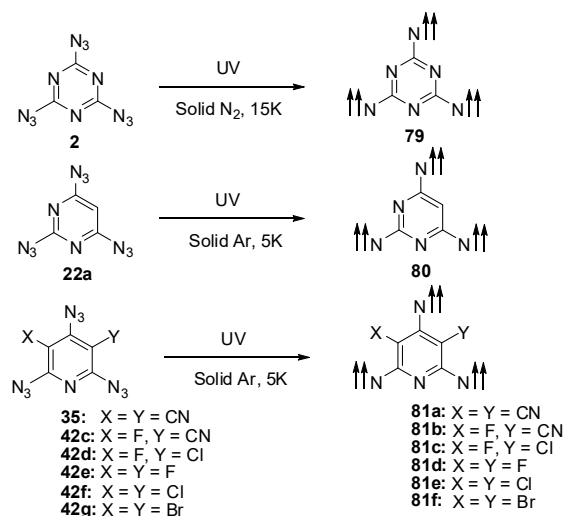
As a rule, the triplet nitrene tensor D_t equals to D_T of triplet nitrene arising as intermediate product during the photolysis of diazidoazine. Using this D_T value derived from EPR spectrum, one can rather precisely calculate D_Q and E_Q of the corresponding quintet dinitrenes.

Theory also predicts, that D_S and E_S of C_{2V} symmetric septet trinitrenes with two magnetically equivalent nitrene units ($D_{t1}=D_{t2}=D_t$) and the third nitrene unit with $D_{t3}=D_t(1+\lambda)$, where $\lambda=(\rho_3-\rho_1)/\rho_1$ and ρ_1 , ρ_2 and ρ_3 are spin densities on the nitrene units, depend on D_t , the angle $\theta=2\alpha$ and parameter λ as shown below:⁷⁰

$$D_S = -D_t(1+\lambda)/10 \quad (3)$$

$$E_S = D_t[4\cos^2\alpha - (1+\lambda)]/30 \quad (4)$$

Extensive EPR studies have shown that septet 2,4,6-trinitreno-1,3,5-triazine **79**⁷¹ obtained by the photolysis of triazide **2** in solid nitrogen has the highest negative parameter $D_S = -0.123 \text{ cm}^{-1}$ and possesses the strongest magnetic properties among all septet trinitrenoazines (Scheme 32). For comparison, the D_S values of septet 2,4,6-trinitrenopyrimidines **80**³² and 2,4,6-trinitrenopyridines **81a-e**⁷²⁻⁷⁷ are equal to -0.112 and -0.102 cm^{-1} , respectively. At the same time, all septet trinitrenoazines are much stronger molecular magnets in respect with septet 1,3,5-trinitrenobenzenes,⁷⁸⁻⁸¹ the D_S values of which do not exceed, as a rule, -0.096 cm^{-1} . All these data demonstrate that *N*-heterocyclic systems with numerous triplet nitrene units in the core are the best molecular magnets among high-spin organic molecules.

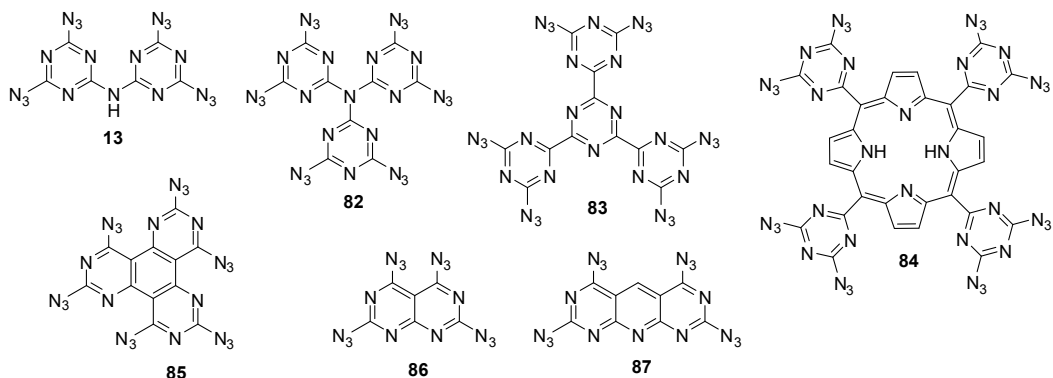


Scheme 32. Photochemical preparation of septet trinitrenes **79**, **80** and **81a-f**.

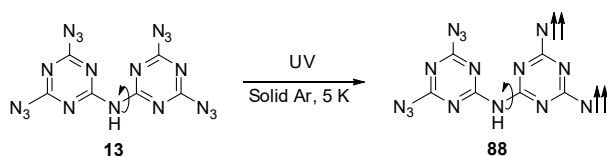
The use of different substituents X and Y in trinitrenes **81a-e** opens up the way to fine tuning of the magnetic parameters D_S and E_S in septet hexaradicals. Moreover, the magnetic characteristics of septet trinitrenes can drastically be changed on introducing heavy atoms as X and Y substituents. Thus, septet trinitrene **81f** has $D_S = +0.297 \text{ cm}^{-1}$ and $E_S = +0.017 \text{ cm}^{-1}$ due to the effect of heavy bromine atoms.⁸² Although trinitrene **81f** with positive D_S does not possess the properties of the molecular magnets, is seven-level molecular spin system may also be of interest for design of some electronic devices.

Up to date, nothing is known about magnetic properties of high-spin nitrenes with four and more nitrene units in the azine ring. Theoretically, these polynitrenes may be obtained by photolysis of hypothetical azides **82-87**, the synthesis of which should not be too problematic (Scheme 33). However, recent EPR studies of the photolysis of tetraazide **13** have shown that only quintet dinitrene **88** is formed in the reaction (Scheme 34).⁸³ The second diazido-substituted triazine ring of compound **13** has inappropriate orientation toward UV light in the argon matrices and remains photochemically inactive. Another sort of problems arises during the photolysis of diazide **89**⁸⁴ and triazide **91**.⁸⁵ In both cases, the photochemical

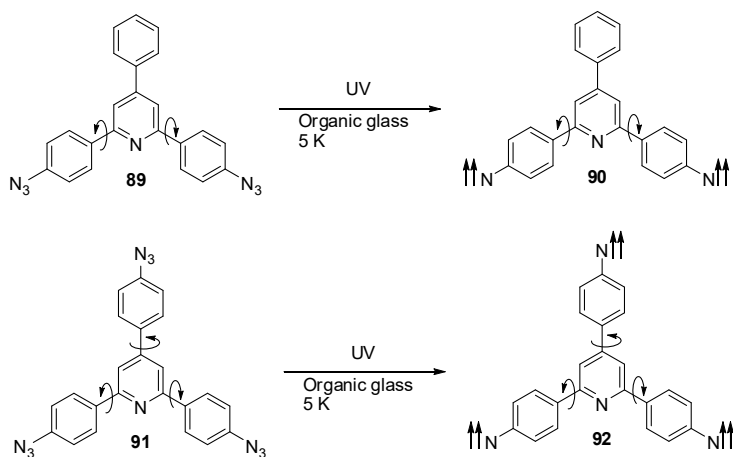
reactions led to the mixtures of rotamers of quintet dinitrene **90** and septet trinitrene **92** as the final products (Scheme 35). These studies have shown that structurally flexible polyazides **13** and **82-84** are not perfect for photochemical preparation of super-high-spin polynitrenes. More promising precursors of super-high-spin organic molecular systems are structurally rigid hexaazide **85** and tetraazides **86** and **87**, provided that all the azido groups of these compounds are easily photolyzed.



Scheme 33. Possible precursors for preparation of superhigh-spin molecules.



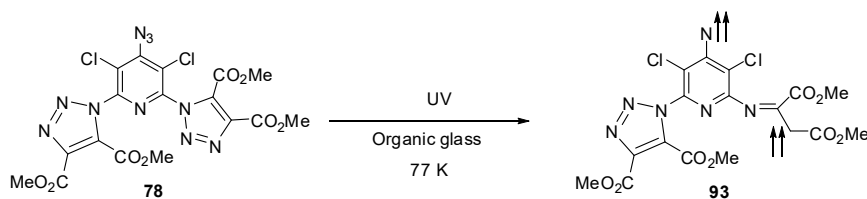
Scheme 34. Photolysis of tetraazide **13**.



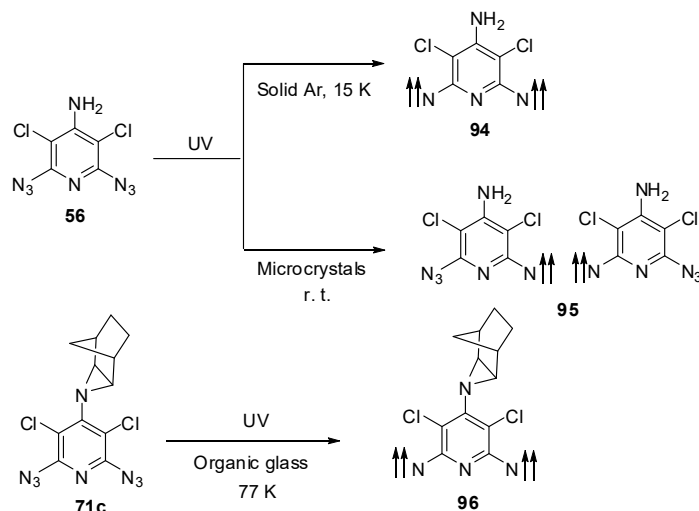
Scheme 35. Photolysis of diazide **89** and triazide **91**.

The reactions of the azido groups of polyazidoazines with reductants, amines, phosphines, phosphites and dipolarophiles provide access to diverse starting compounds used for photochemical preparation of new interesting high-spin polyradicals. Thus, the photolysis of azide **78** in cryogenic matrices allowed the generation of unusual quintet nitrenocarbene **93** (Scheme 36).⁸⁶ Diazides **56** and **71c**, obtained from triazide **42f**, were used for photochemical preparation of quintet dinitrenes **94** and **96** possessing unusually large

magnetic parameters E_Q due to unusually small angles $\Theta \sim 114^\circ$ (see eq. 2) in the molecules of these species (Scheme 37).⁸⁷⁻⁹¹ Moreover, the photolysis of diazide **56** in microcrystals produced stable at room temperature triplet nitrenes existing in the form of quintet spin state pairs **95**.⁹²



Scheme 36. Photolysis of azide **78**.



Scheme 37. Photolysis of diazides **56** and **71c**.

6. Conclusions

Except of very sensitive azides **2**, **8**, **15**, **31** and **33**, all other polyazidoazines are rather safety compounds and can easily be prepared from commercially available precursors in one step in multi-gram quantities. The thermal decomposition of polyazidoazines at various experimental conditions may be used for preparation of a great variety of high-nitrogen heterocyclic systems possessing useful physical and chemical properties. On the other hand, the photochemical decomposition of polyazidoazines in solid phase (e.g., crystals and co-crystals, organic glasses, solid inert gases) allows the preparation of multi-spin heterocyclic systems possessing the record magnetic anisotropy. These systems are of considerable interest for investigations of molecular magnetism and design of quantum computers. Finally, the nonequivalent azido groups of polyazidoazines can selectively react with various reagents thus allowing one to synthesize actually unlimited number of new heterocyclic compounds. All these features suggest that the chemistry of polyazidoazines possesses a huge potential and very promising future.

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