

SYNTHESIS OF NITRO DERIVATIVES OF TRIAZOLES

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Abstract— This paper reviews the synthesis routes of nitro derivatives of triazoles with emphases on those used as energetic materials.

INTRODUCTION

Triazoles and their nitro derivatives have attracted chemist's considerable attention in recent years because of their synthetic value,¹⁻³ their numerous applications⁴⁻²² in medicine and agriculture due to their extensive biological activities, and their successful applications²³⁻²⁸ as photosensitive and energetic materials.

With the development of space programs²⁹ and the deep oil-well drilling,²⁹ new ideal insensitive high explosives (IHE) are needed.²³⁻²⁴ Triazole energetic material, which is extensively studied,³⁰⁻⁴⁰ is one kind of this explosive. As consistent with other energetic materials with high nitrogen content, triazoles nitro compounds possess advantages^{24-27,41,42} of high density, high energy, low sensitivity, and good heat resistance *etc.* The bond length is 1.352 Å for C-N bond, 1.320 Å for N-N bond and 1.094 Å for N=N bond in triazoles, while those of C-C bond and C=C bond are 1.530 Å and 1.330 Å respectively.⁴³ The shorter bond length makes the molar volume of triazole compounds smaller than that of the cyclopentadiene or pyrazole, which is helpful to increase the density of compounds. Besides, the bond angle of C-N=C bond is about 115°, smaller than that of C-C=C bond (about 124°) and close to the average bond angle of five-membered ring (108°).⁴⁴ This is due to the relative equalization of bond angle of nitrogen containing compounds. In addition, the cyclical tension of triazole compounds is rather weaker than that of carbon cyclic compounds or other heterocyclic compounds with low nitrogen contents, and the unshared electron pair of nitrogen atom is involved in the conjugate system of triazole parent compound. This may enhance the aromaticity of the molecule and improve the heat-resistance of the compound. Furthermore, the formation of intermolecular bond is facilitated due to the presence of nitrogen-hydrogen system in the molecule of triazole compounds, and the intermolecular hydrogen bond can impart the triazole compounds a high melting point. As stated above, the nitro derivatives of triazoles may be employed in energetic materials with high energy, high density, low sensitivity and good heat-resistance.^{24-27,36,41} This kind of energetic material has been eagerly expected for a long time. Although triazole compounds are not so resourceful as aromatic compounds, the synthesis of nitro derivatives of triazoles is rather simple, and their production cost is acceptable. In the last two decades, a number of these compounds have been prepared,^{23-27,41} and chemist's interest in them is increasing.

The nitro derivatives of triazoles can be classified to four categories described below.

1. Nitro substituted triazole derivatives

Their synthesis methods include carbon- or nitrogen-nitration,^{2,3,30,45,46} thermal rearrangement^{47,48} of *N*-nitro group to *C*-nitro group, and the conversion of amino group into nitro group by both oxidation⁴⁹ and Sandermayer reaction^{38,50,51} *etc.*

2. Triazole derivatives with polynitro side chains

Dedicated to Professor Alan R. Katritzky on occasion of his 65th birthday.

This kind of compounds can be synthesized mainly by Mannich reaction,⁵²⁻⁵⁷ Michael addition,³⁵ and cycloaddition reaction.⁵³⁻⁵⁷

3. Polynitrophenyl derivatives of triazole

The common ways to prepare these derivatives are aromatic nucleophilic substitution reaction of halogenated polynitrobenzene with various aminotriazoles.^{23,37,38} Sometimes, the salts of nitrotriazoles are also used as nucleophiles.⁵⁸

4. The salts of nitrotriazoles

They can be prepared by neutralization reactions:⁵⁹⁻⁶²

THE PRESENT STATUS OF SYNTHESIS OF NITRO DERIVATIVES OF TRIAZOLES

1H-1,2,4-Triazole was synthesized in the middle of nineteenth century⁶³ but not its nitro derivatives until the beginning of this century.¹ The possibility of applying the nitro derivatives of triazoles as energetic materials was examined even much later on. In 1901, the nitro derivative of 1,2,4-triazolone was synthesized in Germany.¹ In the fifties of this century, the preparation and applications of 3,5-dinitro-1,2,4-triazol were studied in detail in USA.⁵⁰ Later, some work in this aspect was done by some researchers.^{64,65} T. H. Kopman and his co-workers^{31,33-36} have studied and are studying the nitro derivatives of triazoles since the seventies of this century. They have been successful in synthesizing a number of 1,2,4-triazole's derivatives and in using a simple method to form carbon-nitrogen connection between two nitro triazoles. This filled pages of triazole chemistry. Unfortunately few of these compounds has been put into practical uses. In 1984, The Los Alamos Laboratory of USA designed and calculated several triazole compounds, which were difficult to synthesize, in its strategy programs.²² In 1987, the French disclosed the modified synthesis method and properties of 3-nitro-1,2,4-triazol-5-one.^{24,25} This has drawn chemists' close attention internationally. Examination⁶⁴⁻⁶⁶ of the obtained triazole compounds revealed that introduction of energetic groups into the appropriate positions of triazoles can result in an increase of melting point, density, and detonation velocity, but too many energetic groups will lead to an deterioration of properties of triazole compounds. For instance, the melting point and density of 3-picrylamino-1,2,4-triazole are 310°C and 1.936g/ml respectively,⁶⁴ while the melting point of 2-picryl-3-picrylamino-1,2,4-triazole is only 260°C, and its density is also somewhat lowered.⁶⁴ Introduction of two picryl groups into 5,5'-diamino-3,3'-bi-1,2,4-triazolyl results in a compound with a thermal stability of 340°C, but it is decreased to 150°C when two more picryl groups are introduced into the parent compound.⁶⁴

The melting point and density of some synthesized nitro derivatives of triazoles are shown below.

No	Compound	mp(°C)	density(g/ml)	ref.
1	3-Nitro-1-(2,4-dinitrophenyl)-1,2,4-triazole	90~100	/	65
2	1-Picryl-1,2,4-triazole	228	1.70	64
3	3-Picrylamino-1,2,4-triazole	310	1.936	64
4	2-Picryl-3-picrylamino-1,2,4-triazole	260	1.80	64
5	5,5'-Bis(picrylamino)-3,3'-bi-1,2,4-triazolyl	>340 ⁽¹⁾	1.80	64
6	N,N'-Dipicryl-5,5'-bis(picrylamino)-3,3'-bi-1,2,4-triazolyl	150 ⁽¹⁾	1.83	64
7	3,5-Dinitramino-1,2,4-triazole	165	/	66
8	3,5-Dinitro-1,2,4-triazole	98~99.5	/	29
9	3-Amino-5-picrylamino-1,2,4-triazole	275	1.85	64
10	3,5-Dipicrylamino-1,2,4-triazole	272	1.81	64

11 4-Picrylamino-1,2,4-triazole

225

1.73

64

(1) Temperature of the beginning of the first exotherm in DTA at 10°C/min.

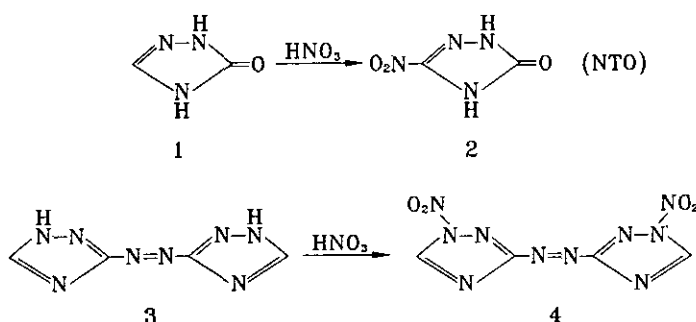
SYNTHESIS METHODS

1. Synthesis of nitro substituted triazole derivatives

1.1. Direct nitration

1.1.1. Nitration with nitric acid

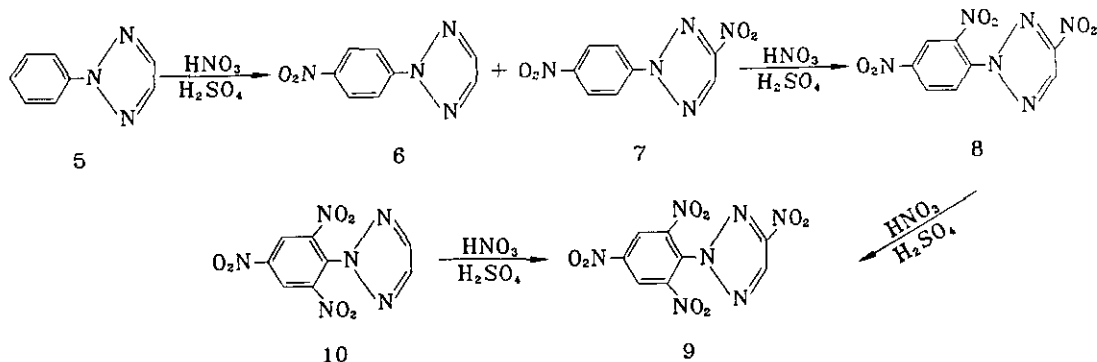
Direct nitration of triazole compounds with nitric acid sometimes gives salts of triazoles.⁶⁷ Nitro derivatives of triazole compounds can be prepared through carbon-nitration or nitrogen-nitration with nitric acid of different concentrations. For example, nitration of 1,2,4-triazol-5-one (TO) (1) or 3,3'-azo-1,2,4-triazol (3) forms 3-nitro-1,2,4-triazol-5-one (NTO) (2)⁶⁸ or 1,1'-dinitro-3,3'-azo-1,2,4-triazole (4)²³ respectively. Acetylation of TO causes its decomposition.⁶⁹ Nitrosation of TO doesn't give any nitroso derivatives, and nitration of TO forms no *N*-nitro compounds.⁶⁶⁻⁶⁸



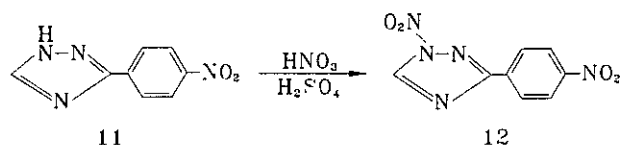
NTO is a new interesting insensitive high explosive, but its high acidity limits its applications.⁷⁰

1.1.2. Nitration with a mixture of nitric acid and sulphuric acid

2-Phenyl-1,2,3-triazole (5) can be conveniently converted into its 2-(4'-nitrophenyl)- or 2-(4'-nitrophenyl)-4-nitro derivatives (6) or (7), which can be further nitrated with mixed acid to give 2-(2',4'-dinitrophenyl)-4-nitro-1,2,3-triazole (8). Additionally the tetranitro derivative (9) can be obtained by nitration of compound (8) or 2-picryl-1,2,3-triazole (10) with mixed acid.²⁹

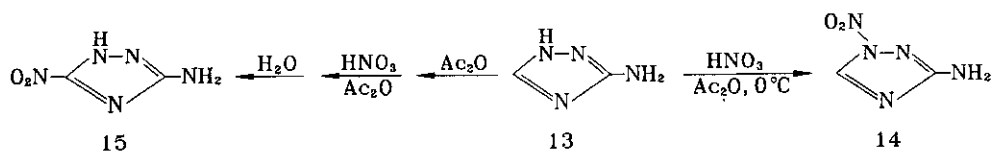


Again, 3-(4'-nitrophenyl)-1,2,4-triazole (11) is nitrated with mixed acid to give 1-nitro-3-(4'-nitrophenyl)-1,2,4-triazole (12).⁷¹

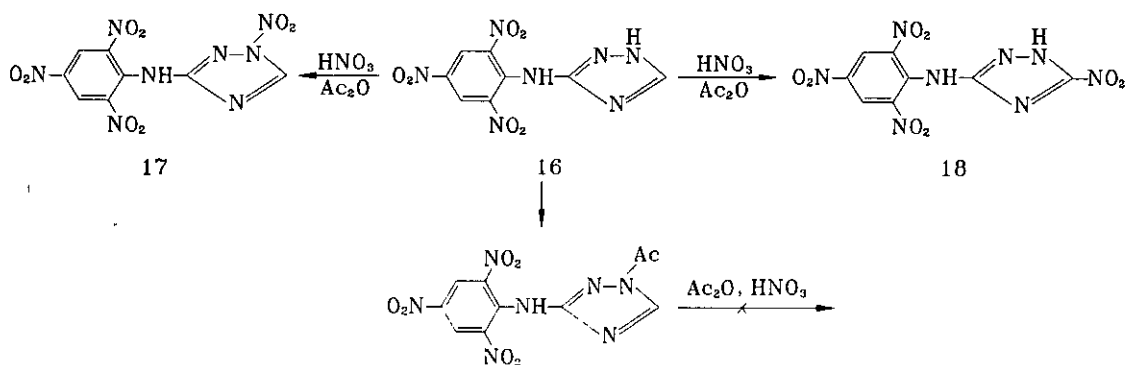


1.1.3. Nitration with a mixture of acetic anhydride and nitric acid

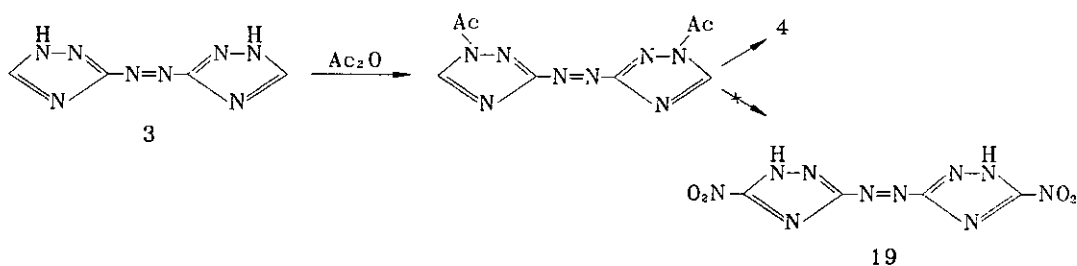
1-Nitro-3-amino-1,2,4-triazole (14) is prepared by nitration of 3-amino-1,2,4-triazole (13) with a mixture of acetic anhydride and nitric acid at 0°C.⁷¹ If the amino group of compound (13) is protected by acetylation, nitration of the acetylated compound gives 3-acetylamino-5-nitro-1,2,4-triazole which can be converted into 3-amino-5-nitro-1,2,4-triazole (15) *via* hydrolysis.⁷²



When 3-picrylamino-1,2,4-triazole (16) is nitrated with a mixture of acetic anhydride and nitric acid, the corresponding *N*-nitro and *C*-nitro derivatives (17) and (18) are obtained. Acetylation followed by nitration does not give any nitro compound.⁶⁹

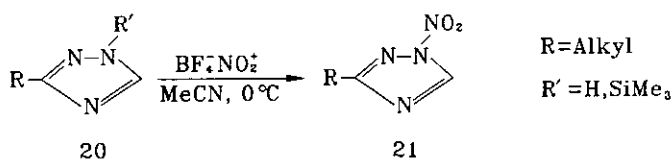


But when 3,3'-azo-1,2,4-triazole (3) is acetylated and then nitrated with acetic anhydride and nitric acid, the resulting product is *N*-nitro derivative (4) instead of the expected *C*-nitro derivative (19).⁷³



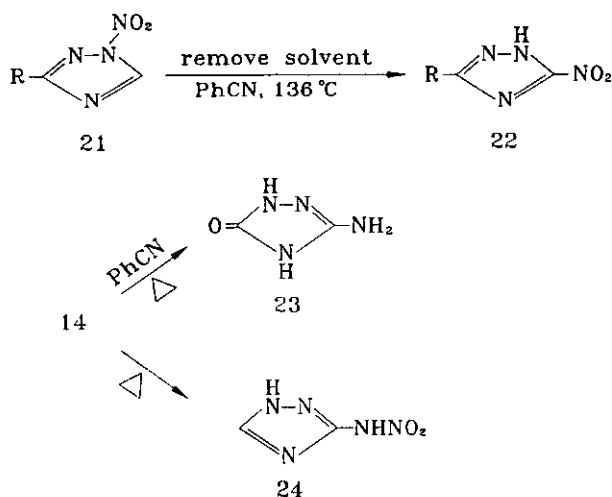
1.1.4. Nitration with nitronium tetrafluoroborate $\text{BF}_4^-\text{NO}_2^+$

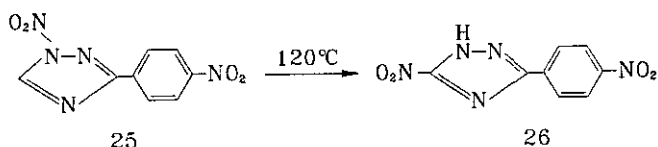
Nitration with this nitrating agent may give cyclic *N*-nitro or *C*-nitro derivatives. For instance, 1,3-disubstituted triazole (20) is converted into *N*-nitro compound (21) and 3-amino-1,2,4-triazole (13) into *C*-nitro derivative (15) through nitration with $\text{BF}_4^-\text{NO}_2^+$.⁷⁴



1.2. Thermal rearrangement from *N*-nitro to *C*-nitro derivatives.

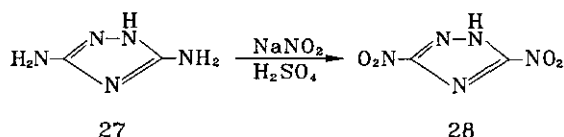
Generally speaking, *C*-nitro derivatives of triazole compounds are more stable than their *N*-nitro derivatives. Direct nitration methods described above can give some *C*-nitro derivatives but in more cases *N*-nitro derivatives are the products. Nevertheless, *N*-nitro of some nitrogen heterocyclic compounds can be changed to *C*-nitro *via* the typical thermal rearrangement. Here are some examples.^{71,74}



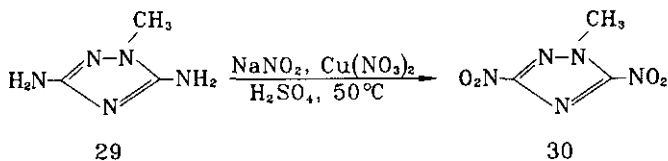


1. 3. Conversion of amino group into nitro group *via* diazotization

Because of the stability of C-nitro group, it is important to synthesize C-nitro derivatives of triazole compounds. A number of triazole compounds contain amino group on their side chains, and amino group can be converted into nitro-group so this conversion provides an useful method for preparation of nitrotriazoles. 3,5-Dinitro-1,2,4-triazole (28) is obtained from 3,5-diamino-1,2,4-triazole (27) by using this method.⁷⁵

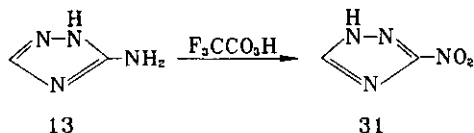


1-Methyl-3,5-dinitro-1,2,4-triazole (30) is prepared from 1-methyl-3,5-diamino-1,2,4-triazole (29) *via* diazotization in the presence of copper nitrate.⁵⁰ The function of copper salts is to retard the hydrolysis of diazonium salts.²⁹



1. 4. Conversion of amino group into nitro group *via* oxidation

Oxidation can convert amino group into nitro group directly. The commonly used oxidant is trifluoroacetic acid. The preparation of 3-nitro-1,2,4-triazole (31) from 3-amino-1,2,4-triazole is an example.⁷⁶

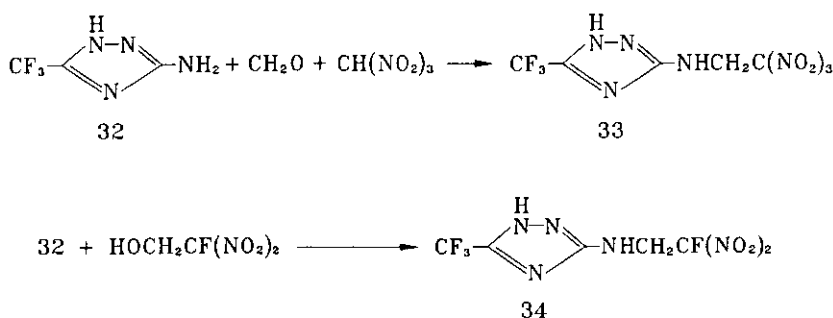


Hydrogen peroxide can also be used as an oxidant. The catalytic oxidation of 3,5-diamino-1,2,4-triazole (27) with hydrogen peroxide in the presence of Na_2WO_4 gives 3-amino-5-nitro-1,2,4-triazole (15).⁷⁷

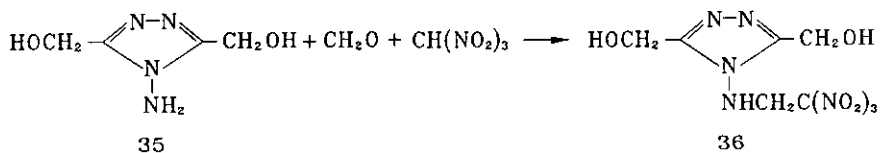
2. Synthesis of triazole derivatives with polynitro side chains

2.1. Mannich reaction

Aminotriazoles can function as a basic component of Mannich reaction because of their basicity, and trinitromethane or the like may be used as acidic components. The electron withdrawing group on the 5-position of 3-amino-1,2,4-triazole can facilitate the Mannich reaction. Thus, condensation of 3-amino-5-trifluoromethyl-1,2,4-triazole (32) with formaldehyde and trinitromethane or with 2-fluoro-2,2-dinitroethanol gives products (33) or (34) with polynitro side chain.⁷⁸

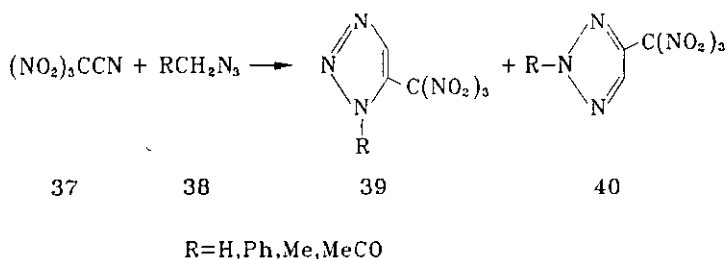


The condensation product (36) of 4-amino-3,5-dihydroxymethyl-1,2,4-triazole (35) with formaldehyde and trinitromethane has also been successfully prepared.⁷⁹



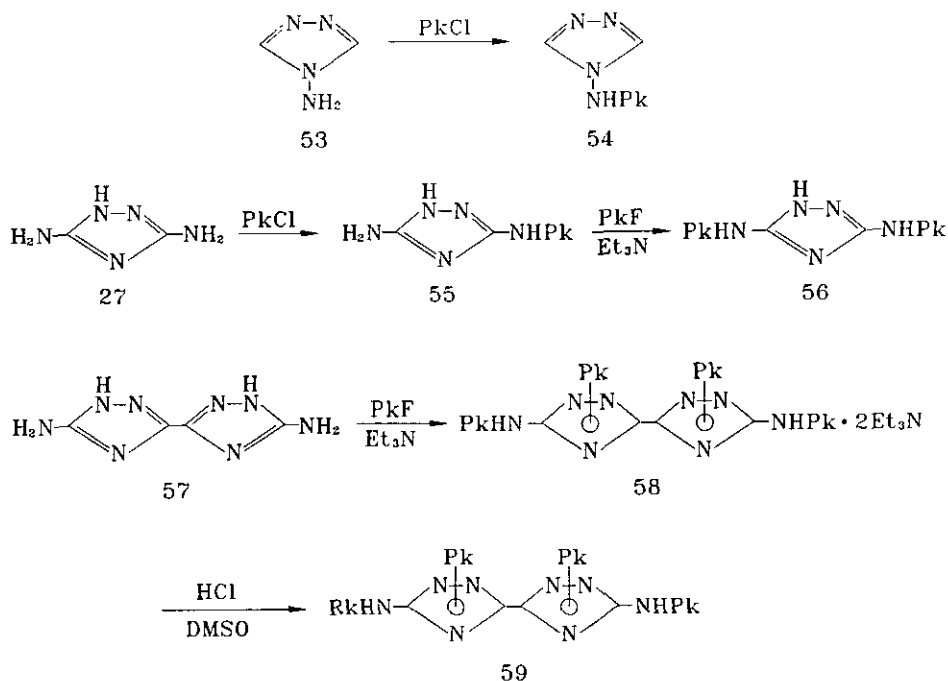
2.2. Cycloaddition reaction

A widely used method^{56-57,80-81} for synthesizing triazole derivatives with polynitro side chains is the cycloaddition reaction of nitrile with diazonium compound or azide. These reactions are usually carried out under hard conditions, but nitrile with electron withdrawing groups, such as trifluoroacetonitrile and trinitroacetonitrile *etc.*, can accelerate the cycloaddition reactions. For instance, trinitroacetonitrile (37) reacts with azide (38) to form 1,2,3-triazole's polynitro-derivatives (39) and (40).^{56,57}

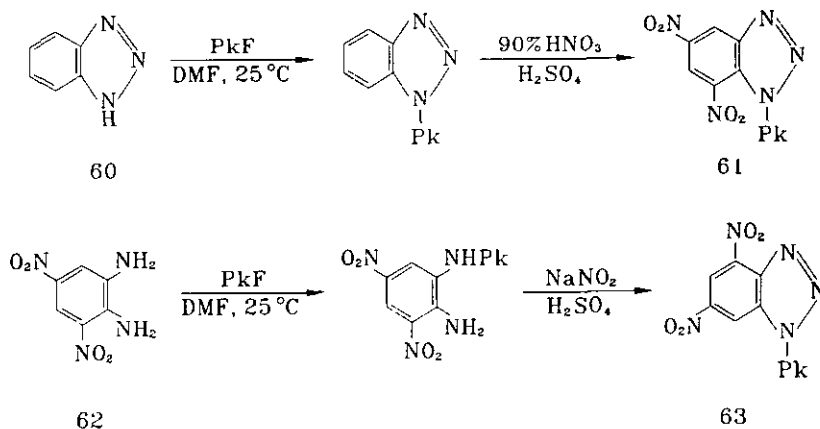


3. Synthesis of polynitrophenyl derivatives of triazoles

given below.⁸³

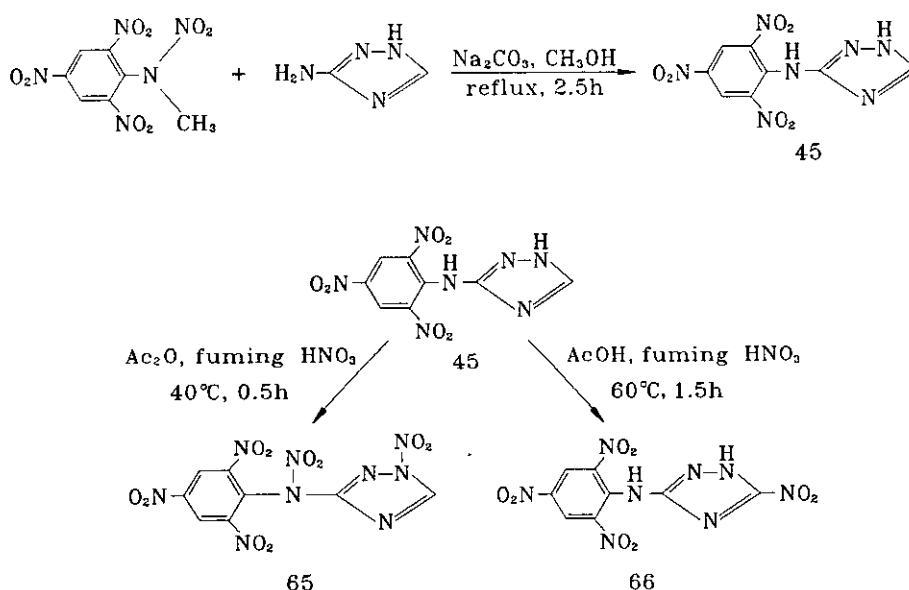


5,7-Dinitro-1-picrylbenzo-1,2,3-triazole (61) (BTX) is a heat resistant initial explosive, which is obtained by the condensation reaction of benzotriazole (60) with picryl fluoride followed by nitration.⁸⁶ This compound's isomer (63) (4,6-dinitro-1-picrylbenzo-1,2,3-triazole) can be prepared by a different way-reaction of 3,5-dinitro-1,2-diamino benzene (62) with picryl fluoride followed by diazotization and cyclization.⁸⁶

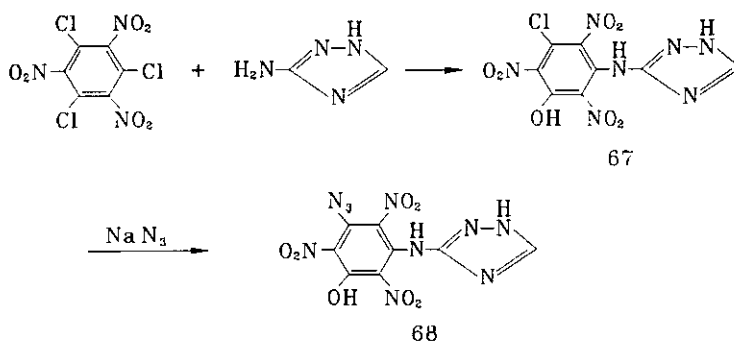


Recently, our laboratory modified the preparation of 3-picrylamino-1,2,4-triazole (45) by using methylnitroamino

group as leaving group and obtained the nitration products (65) and (66) of compound (45).^{68,73}



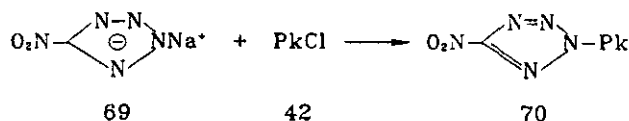
Compound (66) can also be obtained by the reaction of 3-amino-5-nitro-1,2,4-triazole (15) with picryl fluoride.⁷³ We have also tried the reactions of a number of halogenated polynitrobenzene (including 1,3-dichloro-2,4-dinitrobenzene, 1,3-dichloro-2,4,6-trinitrobenzene, 1,3,5-trichloro-2,4,6-trinitrobenzene, and 3-chloro-2,4,6-trinitrophenylmethylnitramine *etc*) with aminotriazole, but only compound (67) has been identified and it can react with sodium azide to offer compound (68).⁷³



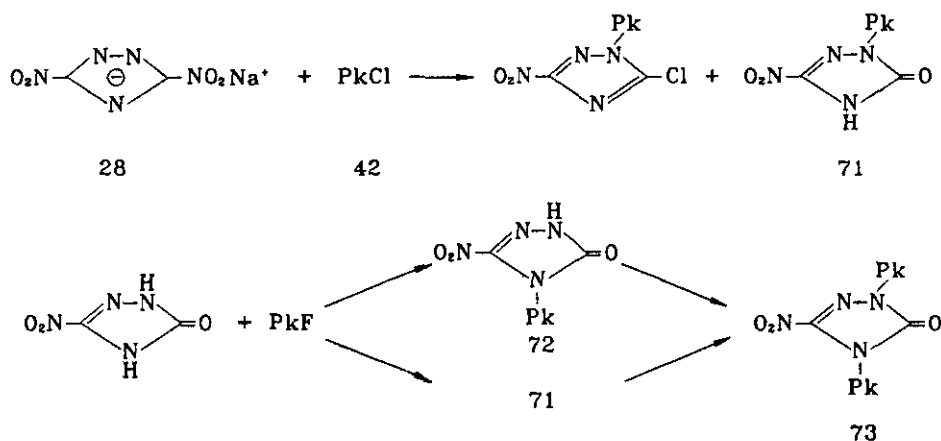
3. 2. Reaction of halogenated polynitrobenzene with salt of nitrotriazoles

It is rather difficult to introduce nitro group to C-atom of triazole ring attaching picryl group. But some salts of nitrotriazole may be used as nucleophiles to react with picryl halide for synthesis purposes. A successful example is the

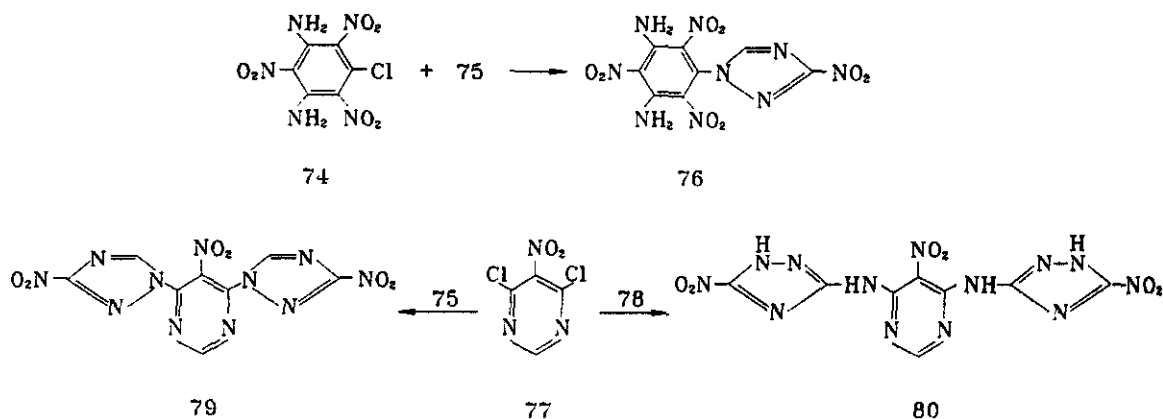
synthesis of compound (70) *via* the reaction of picryl chloride (42) with sodium nitrotetrazole (69).⁵⁷



In 1978, Sitzmann⁵⁷ tried to get a picryl derivative of 3,5-dinitro-1,2,4-triazole (28) by the reaction of picryl chloride (42) with potassium salt of compound (28). He didn't succeed. But he obtained compound (71) which is a picryl derivative of 3-nitro-1,2,4-triazol-5-one (2).⁵⁷ Compound (71) was also prepared *via* the reaction of picryl chloride (42) with potassium salt of compound (2). In 1990, Coburn reported the synthetic methods of compounds (71), (72) and (73).⁵⁸



The preparation and properties of compounds (76), (79) and (80) were reported in 1989.^{54,59,60} Compound (76) was synthesized by the reaction of 3,5-diamino-2,4,6-trinitrochlorobenzene (74) with alkali metal salt of 3-nitro-1,2,4-triazole (75), while compound (79) and (80) were prepared by the reactions of 5-nitro-4,6-dichloropiperazine (77) with compound (75) or with alkali metal salt of 3-amino-5-nitro-1,2,4-triazole (78) respectively.



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