Synthesis of benzannelated five-membered heteroaromatic compounds from 2,4,6-trinitrotoluene

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Dedicated to Professor A. F. Pozharsky on the occasion of his 70th birthday

Abstract

Methods for the synthesis of five-membered benzannelated heterocyclic compounds from the military explosive 2,4,6-trinitrotoluene (TNT) are summarised. The general approach concerns the transformation of the TNT methyl group followed by either intramolecular substitution of the *ortho*-nitro group or regioselective substitution of the *ortho*-nitro group by an appropriate nucleophile and subsequent cyclization.

Keywords: 2,4,6-Trinitrotoluene, benzannelated five-membered heterocycles, nitro group, nucleophilic substitution, cyclization

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1. Introduction

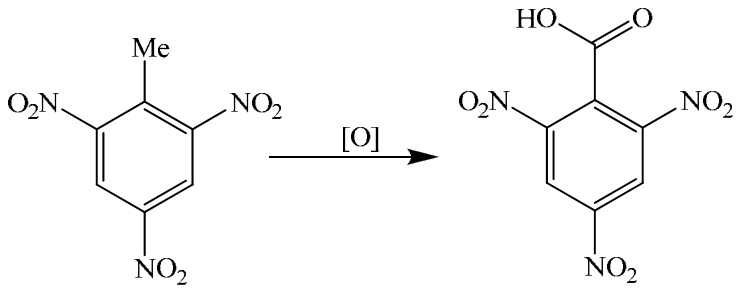
2,4,6-Trinitrotoluene (TNT) is the most mass-scale military explosive. Its industrial production started at the end of the 19th century, and during World War I TNT became a conventional explosive in the belligerent armies. TNT applications greatly extended during World War II, and its production capacity drastically built up.[1] TNT has been in the focus of a great number of publications in the scientific literature. Most of these relate to the explosive characteristics of TNT and its mixtures with other compounds. Relatively fewer papers have so far directly addressed TNT chemistry, although their absolute number is quite significant.[2] However, systematic researches on TNT chemical transformations have been lacking, except for the generation of stable σ-complexes through the nucleophilic addition to the TNT aromatic cycle.[3] Only during the last 10-15 years, judging from a great number of publications, have comprehensive studies of TNT chemistry, focused on TNT transformations to readily available multi-purpose raw materials, been undertaken. This review discusses a single aspect of TNT transformations — the preparation of TNT-sourced dinitro benzannelated five-membered aromatic heterocycles. This has been the most closely researched area of TNT transformations until now. To avoid duplication in describing syntheses of benzannelated heterocycles the review provides the introductory sections that address TNT reactions by the methyl group and reactions involving TNT nitro groups.

Caution: polynitroaromatic compounds (TNT and products of its transformations) are explosive; proper precautions and protective equipment (shields, glasses) should be used during even small-scale experiments.

2. Discussion

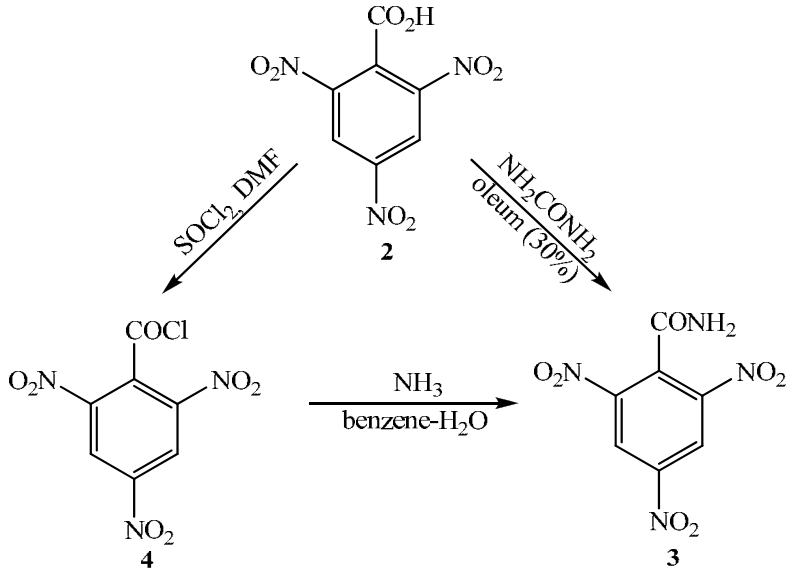
2.1. Reactions of the TNT methyl group

An important TNT reaction is its oxidation. Resulting 2,4,6-trinitrobenzoic acid **2** and its functional derivatives (amides, haloanhydrides, and nitrile) are of interest as starting molecules in the synthesis of polyfunctional heteroaromatic compounds.

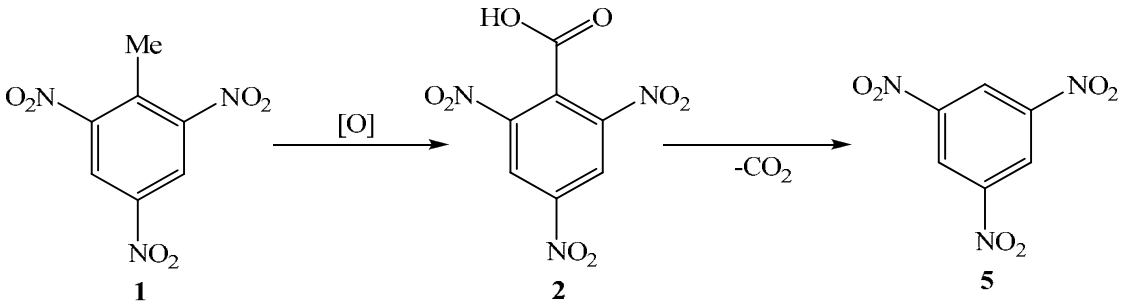


1 **2**

It is known that 2,4,6-trinitrobenzoic acid can be prepared by TNT oxidation using various oxidants such as HNO_3[4a] and $Na_2Cr_2O_7$[4b] as well as by electrolytic oxidation.[4c] TNT oxidation by $K_2Cr_2O_7$ in H_2SO_4 is a preparative technique to produce this acid.[5] A process technology of TNT oxidation by nitric acid at high temperature and pressure is reported.[6] The treatment of the intermediate acid with $SOCl_2$ (or PCl_5) leads to respective acid chloride, and the latter reacts with aqueous ammonia solution to give 2,4,6-trinitrobenzoic acid amide.[7] Another approach to preparing the amide is a reaction of 2,4,6-trinitrobenzoic acid with urea. The reaction runs in 30% oleum.[7] Such method allows preparing the amide in a higher yield (90%) than by the acid chloride treatment with NH_3 (58%).

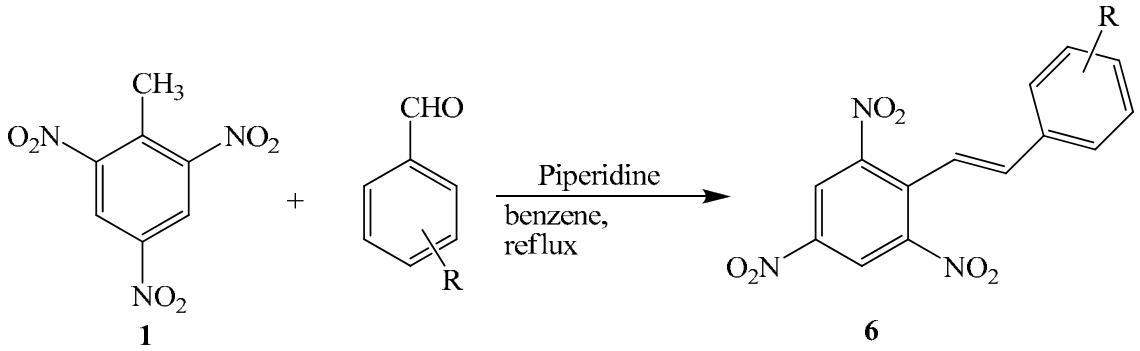


Another TNT derivative, which is no less important, is 1,3,5-trinitrobenzene (TNB). TNB is a multi-purpose synthon, including use for the synthesis of polyfunctional benzannelated heterocycles.[8-11] TNB is prepared by decarboxylation of 2,4,6-trinitrobenzoic acid.[5,12]

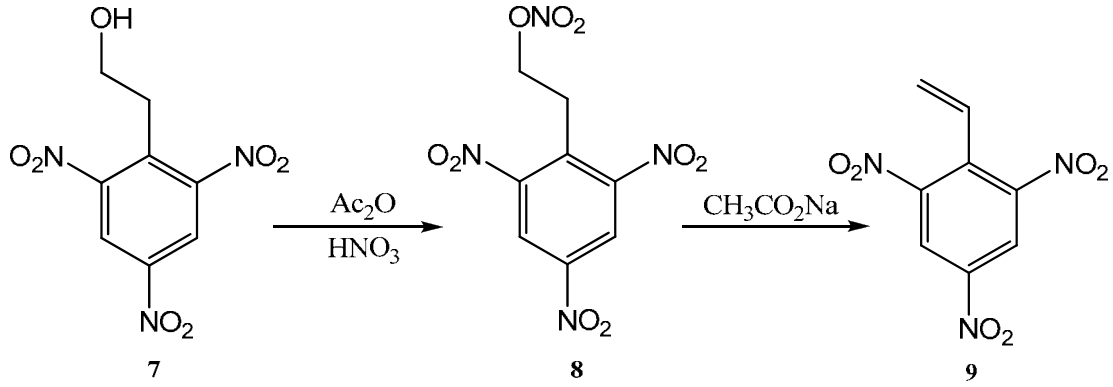


The TNT methyl group is CH-active and able to condense with various aromatic electrophiles, predominantly in the presence of bases (TNT acidity: $pK_a^{H_2O}$= 13.6; $pK_a^{CH_3OH}$=15.6; pK_a^{DMSO}= 10.5).[13]

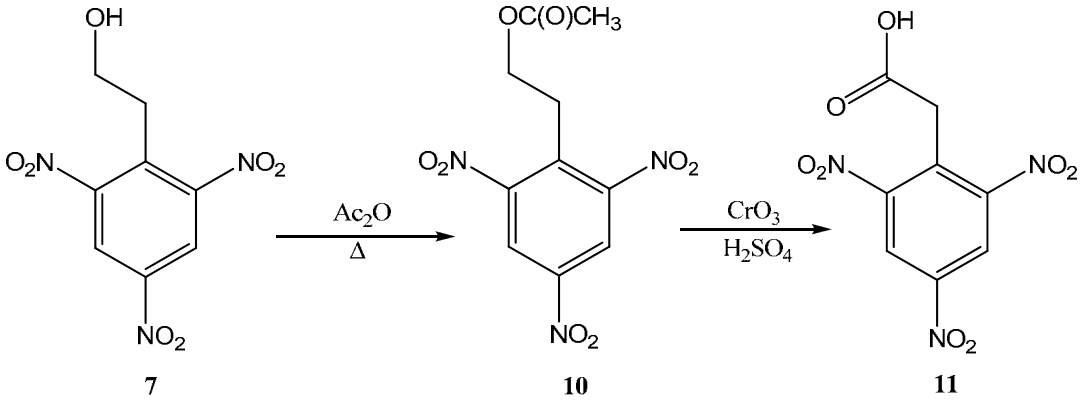
Among the most well-known TNT reactions by the methyl group is reaction with aromatic aldehydes leading to stilbene derivatives. Ullmann and Pfeiffer were the first to study these reactions back in the early 20th century.[14,15] TNT condensation with aromatic aldehydes proceeds on refluxing the components in the benzene medium in the presence of a catalytic amount of secondary amine (piperidine, morpholine or diethylamine). In addition to benzaldehyde derivatives, their heteroaromatic analogs also react in these conditions.[16-18] These stilbenes have been lately shown to be important semi-products in the 4,6-dinitroindole synthesis.[18]



TNT reacts with aliphatic aldehydes by the aldol type to yield corresponding alcohols. Heating of TNT with formalin or in a formalin-THF mixture under reflux leads to picrylethanol in a nearly quantitative yield.[19] Picrylethanol, as affected by Ac_2O-HNO_3, generates nitrate **8**, which under the action of CH_3CO_2Na transforms to 2,4,6-trinitrostyrene **9**.[20]

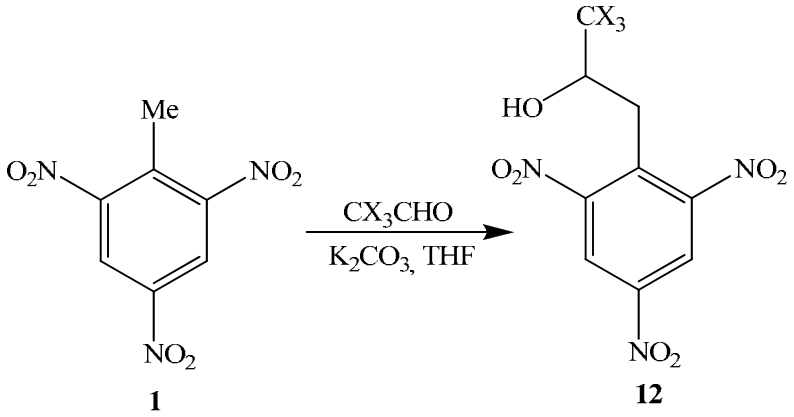


Also, 2,4,6-trinitrophenylethanol **7** reacts with acetic anhydride to give 2,4,6-trinitrophenylethylacetate **10**. The latter is a convenient starting compound for preparation of trinitrophenylacetic acid **11**.[21]



7 **10** **11**

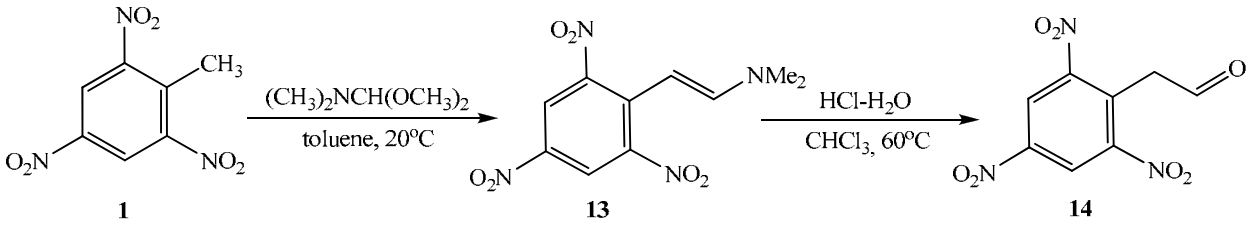
A reaction with fluoral and chloral is another example of the TNT interaction with aliphatic aldehydes.[22] The reaction runs smoothly under reflux in THF in the presence of K_2CO_3.



1 **12**

X=F, Cl

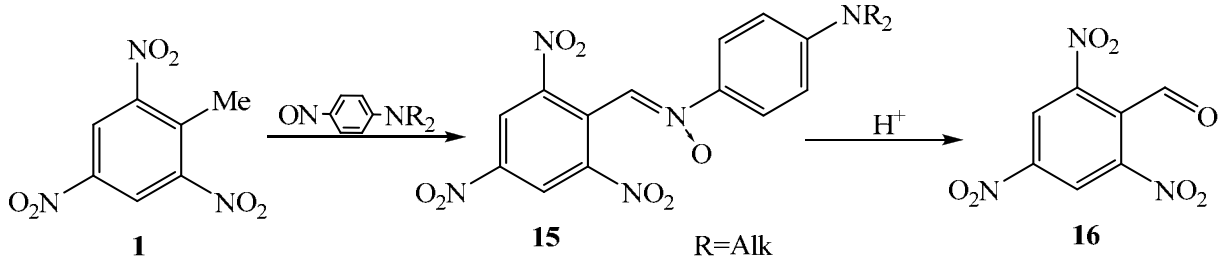
A TNT reaction with dimethylformamide dimethylacetal (DMF DMA) gives an opportunity to synthesize a broad variety of polynitro benzannelated heterocyclic compounds. Of note are mild conditions of the TNT reaction with DMF DMA (in toluene at 20°C).[23] A synthesis of 2,4,6-trinitrophenylacetaldehyde **14** was designed on the basis of enamine **13**.[23] This compound is a convenient synthon for the annelating of additional heterocyclic moieties.



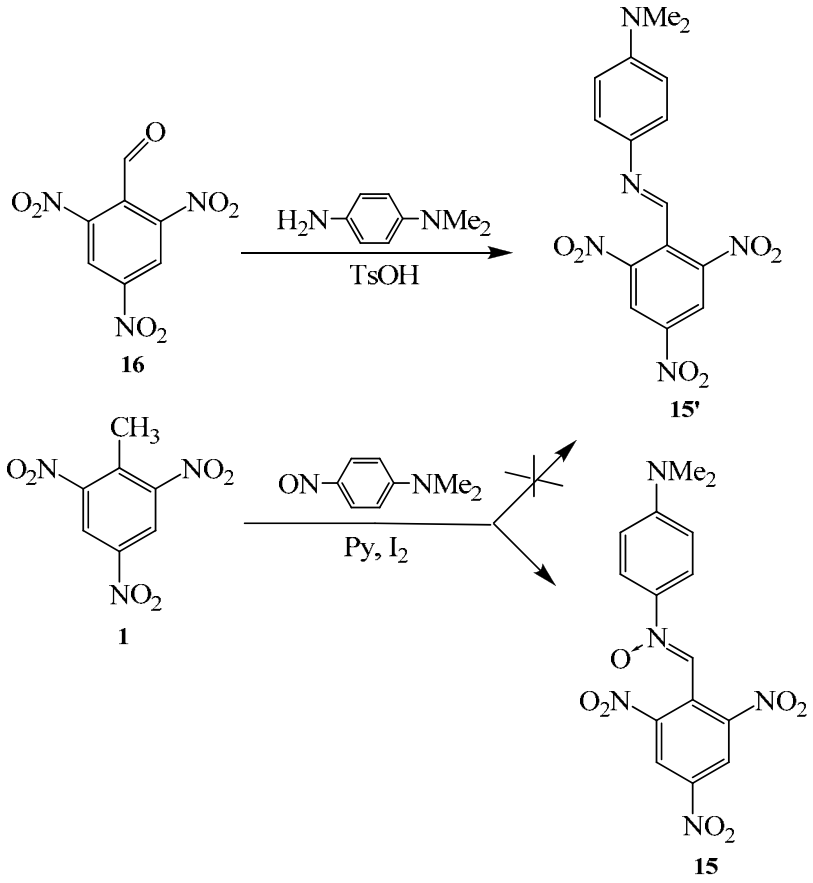
1 **13** **14**

2,4,6-Trinitrobenzaldehyde is another TNT derivative with an extensive synthetic potential. The method was described for the first time by Sachs and Everding[24] and was optimized

repeatedly afterwards.[25,26] TNT reacts with *p*-nitrosodialkylanilines to generate nitrones **15**,[27] which yield 2,4,6-trinitrobenzaldehyde **16** in the acidic hydrolysis conditions.

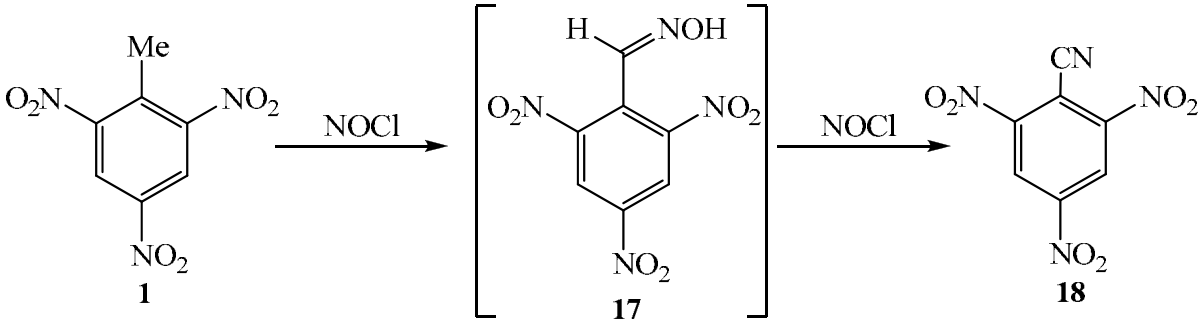


Note that for a long time compound **15** (R=Me) was assumed to have a different structure, i.e. that of azometin **15'**.[24-26,28] However, it has recently been established that this compound is a nitrone. The interaction of trinitrobenzaldehyde with 4-(*N*,*N*-dimethylamino)aniline has been shown to lead to compound **15'** that differs from a product of TNT condensation with 4-nitroso-(*N*,*N*-dimethyl)aniline (NMR and mp data).[27] It is known from older researches that condensation of nitrotoluenes with nitroso compounds results in *N*-oxides.[29-31] A comparison of all the foresaid facts led to the conclusion that the product of TNT condensation with nitrosodimethylaniline is nitrone **15**.



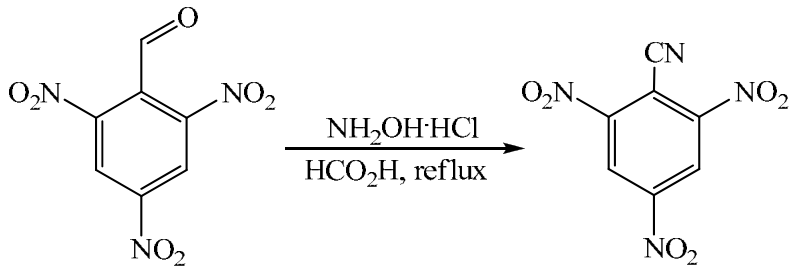
Imines, similar to compound **15'**, are generated in a reaction between trinitrobenzaldehyde **16** and aromatic amines. The reaction is performed either by boiling in benzene in the presence of TsOH in catalytic amounts[28] or in boiling MeOH.[32]

2,4,6-Trinitrobenzonitrile **18** is produced by the TNT treatment with nitrosyl chloride via the 2,4,6-trinitrobenzaldoxime as an intermediate.[33]



1 **17** **18**

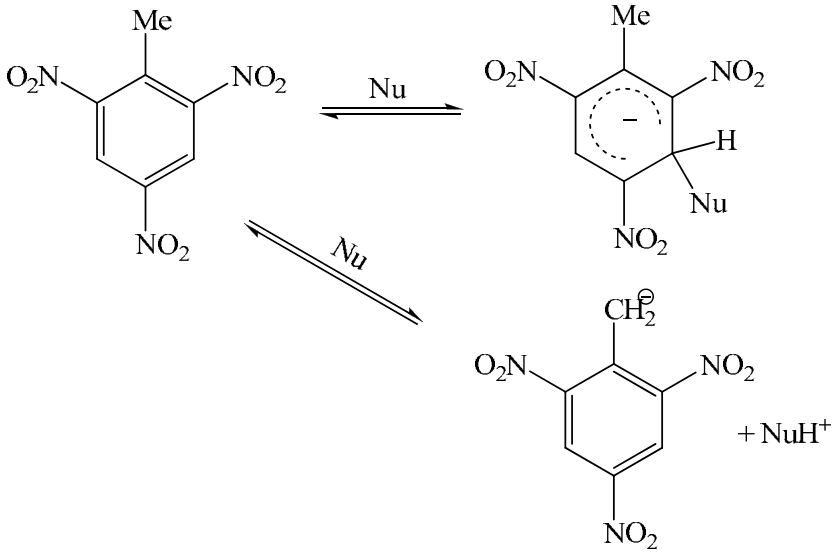
A method of trinitrobenzonitrile synthesis from trinitrobenzaldehyde has been described. The treatment of aldehyde **16** with hydroxylamine hydrochloride in formic acid results in nitrile **18**.[34]



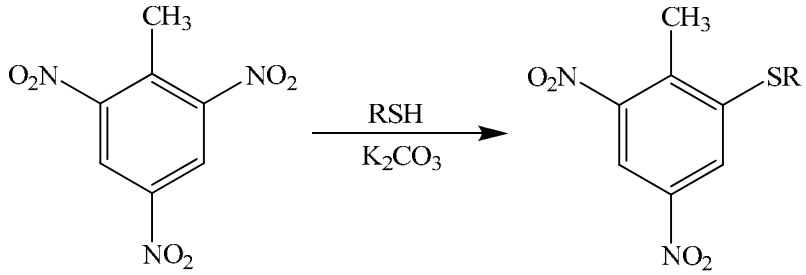
16 **18**

2.2. Transformations of the nitro group

Stable anion σ-complexes are normally formed under the action of O-, S-, N-, P- and C-nucleophiles and hydride ions on TNT due to nucleophilic addition to the aromatic cycle, usually to the C(3) atom. Further on, in case of considerably basic nucleophiles (alcoholates, stabilized carbanions, and amines) in a slower stage the proton splits off from the TNT methyl group and the 2,4,6-trinitrobenzyl anion is generated.[3,35]

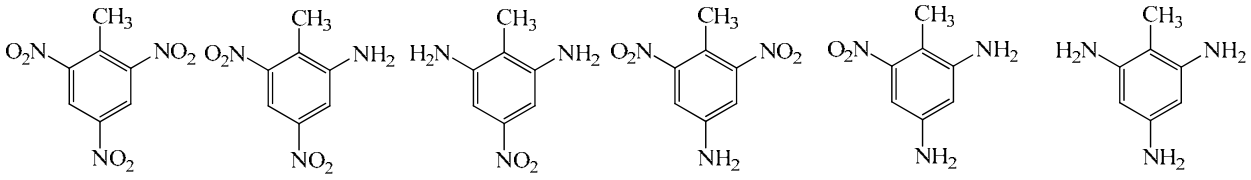


Regioselective substitution of the *ortho*-nitro group occurs during heating TNT with aromatic and aliphatic thiols in the presence of inorganic bases in aprotic dipolar solvents.[6,36-38]



1 **19**

TNT derivatives with reduced nitro groups are also of interest as possible semi-products to prepare bicyclic systems. Currently there are methodologies that allow selective reduction of the nitro group in TNT.[39-42]

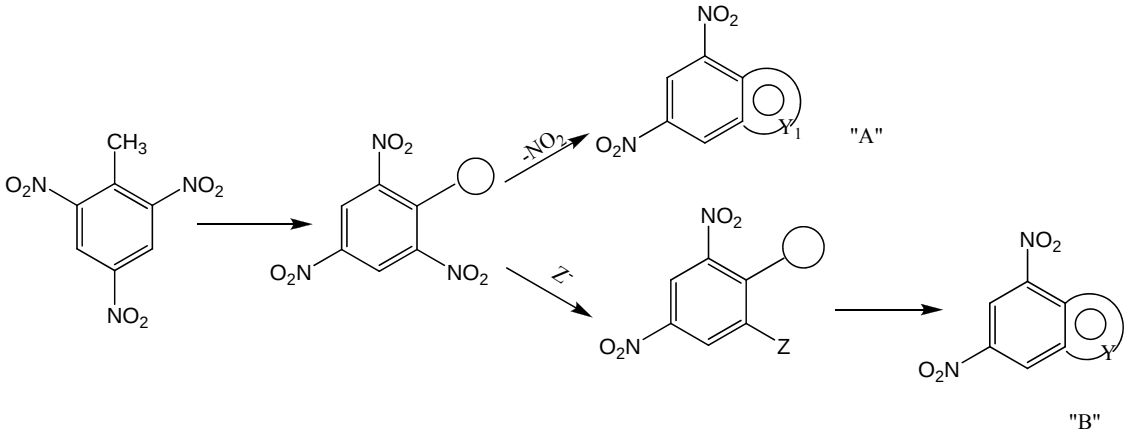


TNT

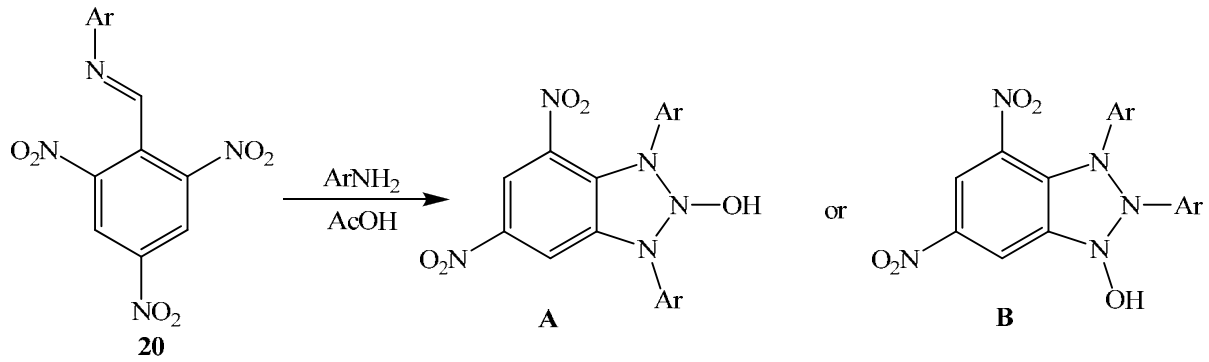
2.3. Synthesis of five-membered benzannelated heterocyclic compounds

A strategy for the synthesis of five-membered benzannelated heterocycles builds on the transformation of the 2,4,6-TNT methyl group followed by either intramolecular substitution of

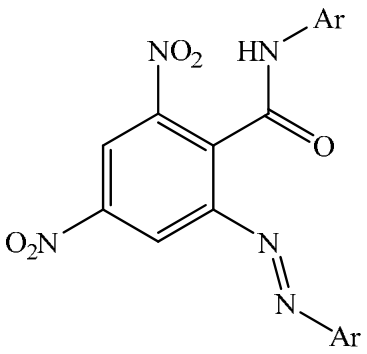
the *ortho*-nitro group (Variant A) or regioselective substitution of the *ortho*-nitro group by an appropriate nucleophile and subsequent cyclization (Variant B).



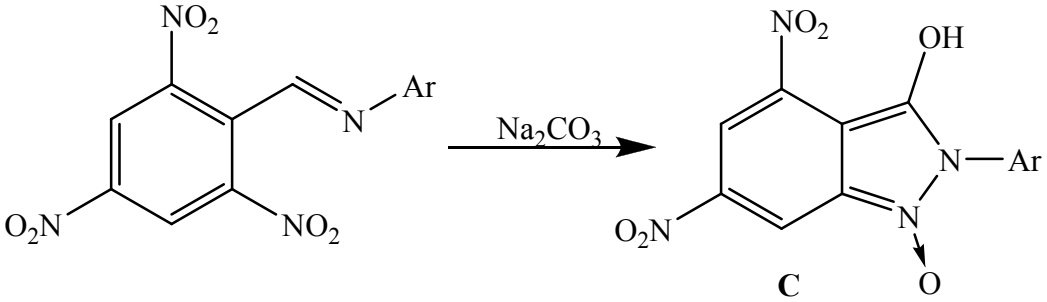
A number of older publications describe synthetic approaches to some compounds on the basis of TNT derivatives, which were assumed to have a structure of 4,6-dinitrobenzannelated heterocycles. Recently after the application of advanced physical-chemical methods for the structure identification, it appears that these data needed additional verification. For instance, azometins **20** are known to readily react with arylamines in boiling acetic acid to give individual compounds, which were earlier assigned either the **A** or **B** structure.[43-46]



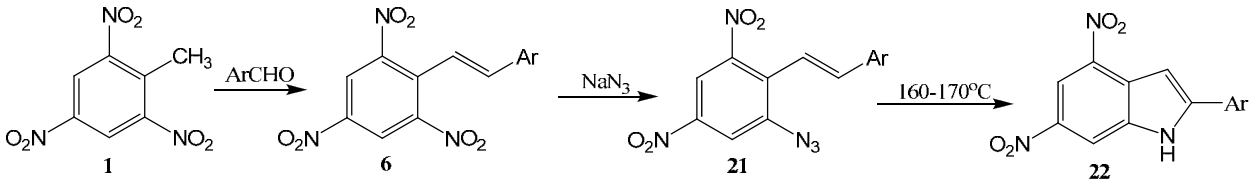
This reaction has recently been examined in more detail. The structure of the reaction products was proved using X-ray analysis (XRA). It was established that the earlier assumptions regarding the structures **A** and **B** had been incorrect.[47] The synthesized compounds proved to be *N*-aryl-2-arylazo-4,6-dinitrobenzamides.



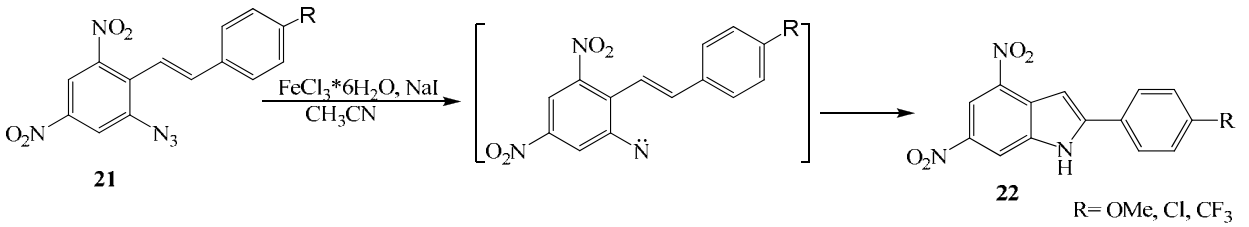
Another series of researches communicated at the beginning of the 20th century deals with cyclization of azometins **20** to derivatives of 3-hydroxy-4,6-dinitroindazol-*N*-oxides **C**. The reaction was performed in the presence of Na_2CO_3 in boiling ethanol.[48-50] However, when the review's authors attempted to reproduce the methodology it appeared that the reaction conditions needed clarification.



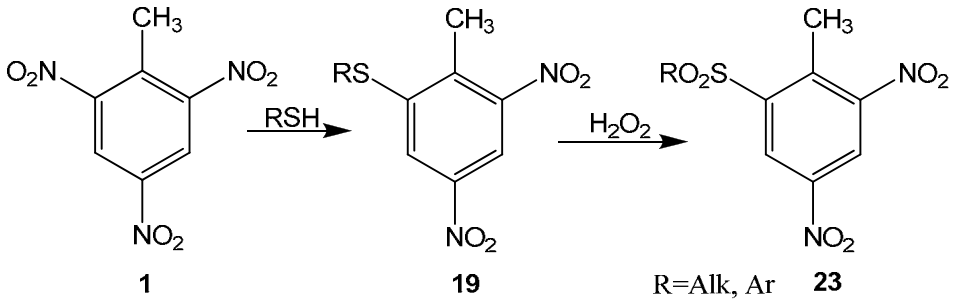
2.3.1. Synthesis of benzannelated five-membered heterocycles with one heteroatom. A TNT-based synthesis of earlier unavailable 2-aryl and 2-hetaryl-4,6-dinitroindoles has been developed.[18] Only *ortho*-NO_2 is substituted under the action of NaN_3 in stilbenes resulting from TNT condensation with aromatic and heteroaromatic aldehydes, and azides **21** are generated. These upon thermolysis give indoles **22** in high yields.



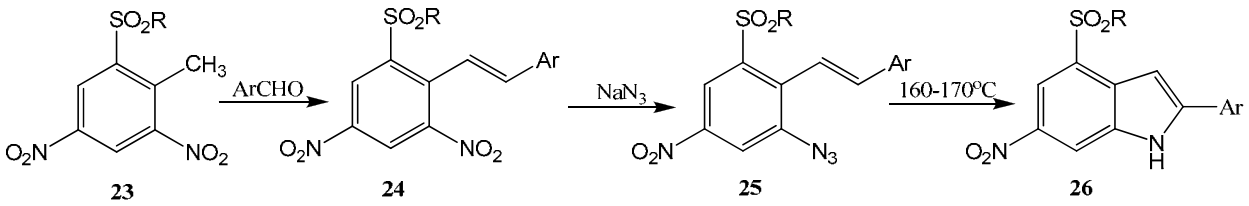
A recent paper proposes another method that allows the preparation of indoles **22** from azides **21** in an even higher yield (>80%).[51] The azides react with the system $FeCl_3*6H_2O$ – NaI in mild conditions (room temperature) to give indoles **22**.



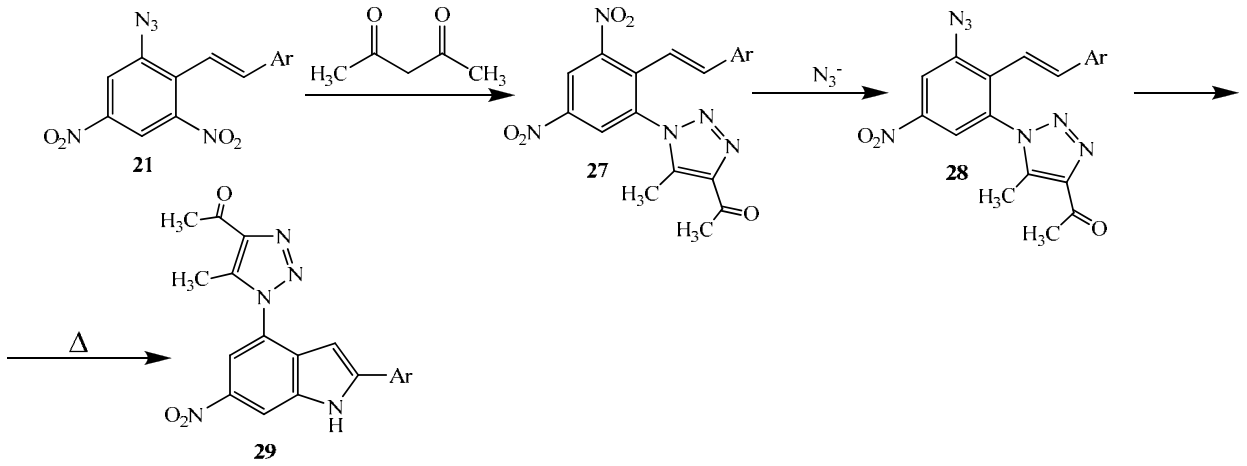
Also, the literature communicates a few approaches to the synthesis of 4-X-6-dinitroindoles (X = R-sulfonyl, 1,2,3-triazolyl). The first approach proposes to prepare 2-R-sulfonyl-4,6-dinitrotoluenes through substitution of the ortho-nitro group with aromatic or aliphatic thiol and oxidation of the obtained sulfide to sulfone.[52]



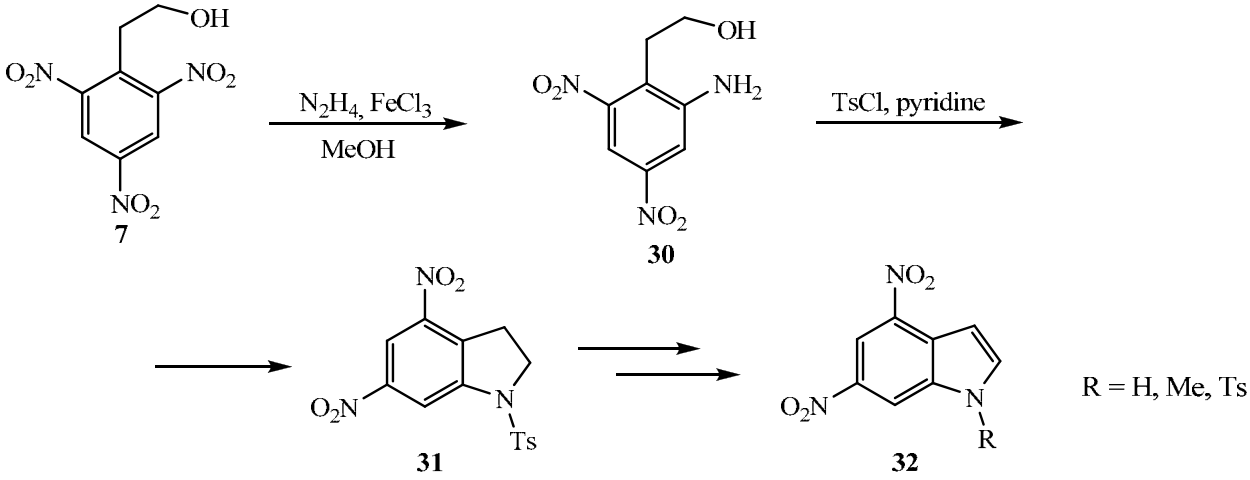
Sulfones **23** undergo condensation reaction with aromatic aldehydes. The *ortho*-nitro group in the formed stilbenes **24** is selectively substituted by the azido group, and the thermolysis of azides **25** leads to 2-aryl-4-(R-sulfonyl)-6-nitroindoles **26**.



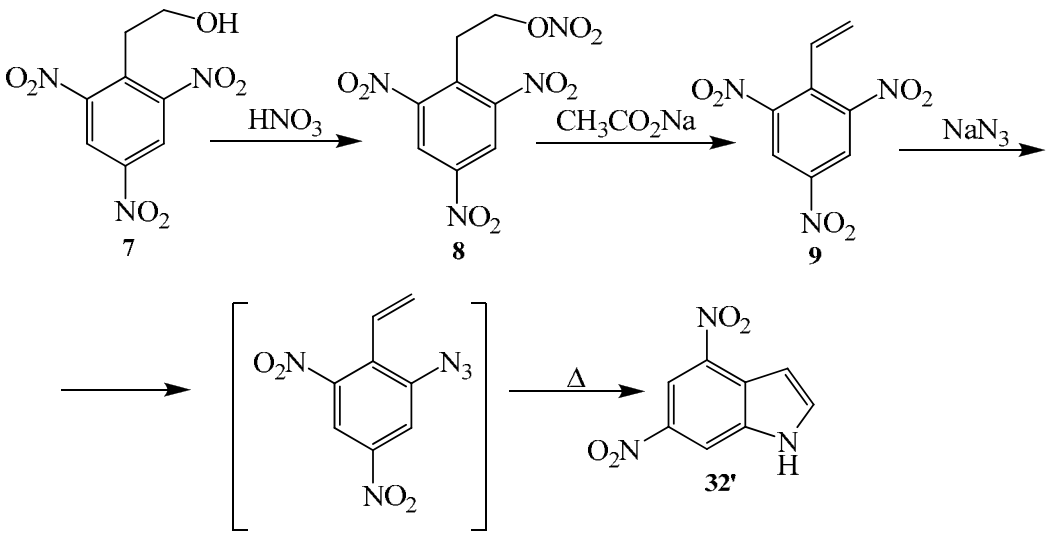
The synthesis of indoles containing a triazole moiety in position 4 suggests that 2-azido-4,6-dinitrostilbenes should be used as initial molecules[53] and comprises their introduction to 1,3-dipolar cycloaddition, substitution of the *ortho*-nitro group in the obtained 2-(*N*-1,2,3-triazolyl)-4,6-dinitrostilbenes for the azido group, and the thermolysis of the synthesized products.



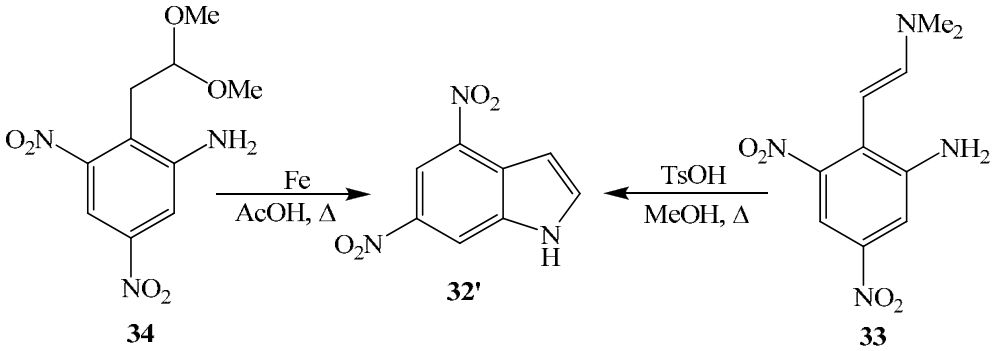
4,6-Dinitroindoles can also be prepared on the basis of picrylethanol.[54,55] Here two approaches to the target product synthesis are possible. In the first case,[54] the *ortho*-nitro group in the initial alcohol **7** is reduced selectively. Amino alcohol **30**, when treated with *p*-toluenesulfochloride, cyclizes to 2,3-dihydro-4,6-dinitro-1-tosylindole **31**. The latter is readily oxidized by air oxygen to give indole **32**.



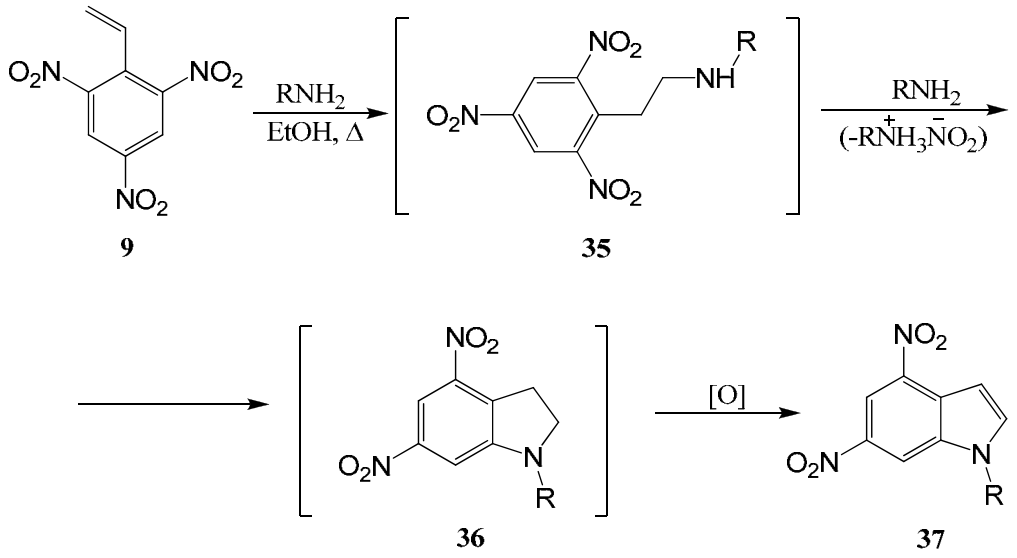
In[55] the authors used an approach based on the picrylethanol transformation to nitrate that was readily denitrated under the action of sodium acetate to produce 2,4,6-trinitrostyrene **9**. The *ortho*-nitro group in the latter is selectively substituted by the azido group, and the thermolysis of azide leads to 4,6-dinitroindole **32'**.



4,6-Dinitroindole can be prepared on the basis of 2-amino-4,6-dinitrotoluene through the interaction with dimethylformamide dimethylacetal. Resulting β-(*N*,*N*-dimethylamino)-2-amino-4,6-dinitrostyrene cyclizes to 4,6-dinitroindole under the action of TsOH.[56]

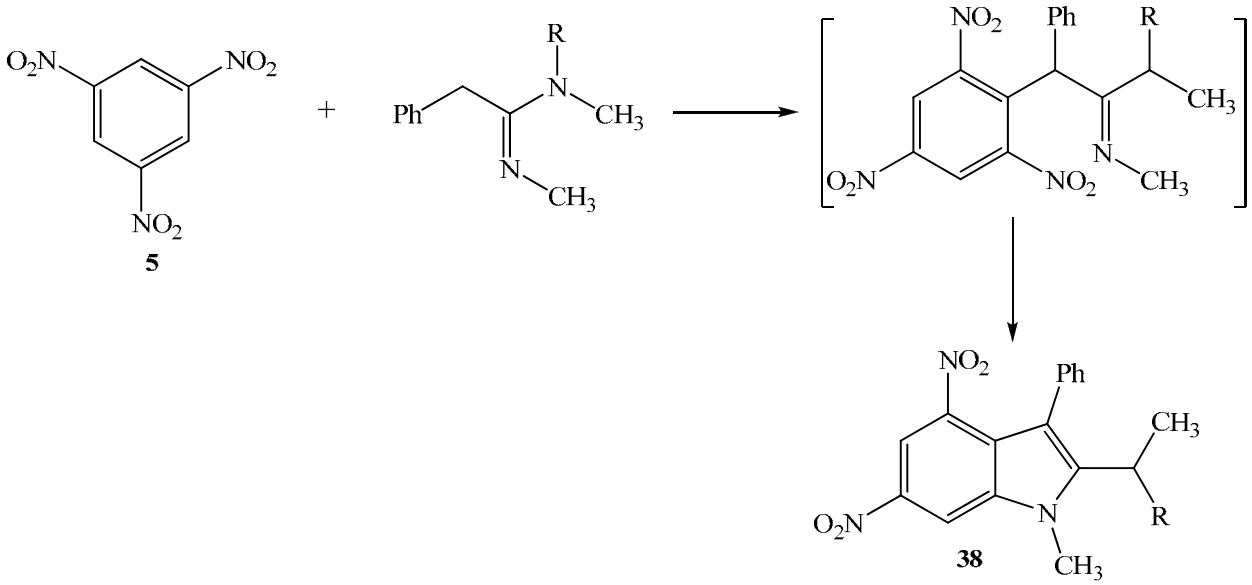


An alternative method proposed by the authors for preparing 4,6-DNI consists of *ortho*-nitro group reduction in picrylacetaldehyde dimethylacetal **34.**[56] The unexpected generation of 1-R-4,6-dinitroindoles was detected in a reaction between 2,4,6-trinitrostyrene and primary amines.[57] In the first step, the amine undergoes addition by the double bond yielding adduct **35** where intramolecular substitution of the nitro group occurs to give indoline **36**. The indoline is oxidized by the nitro compounds present in the reaction mixture and indole **37** is produced in 12-18% yield.[57]

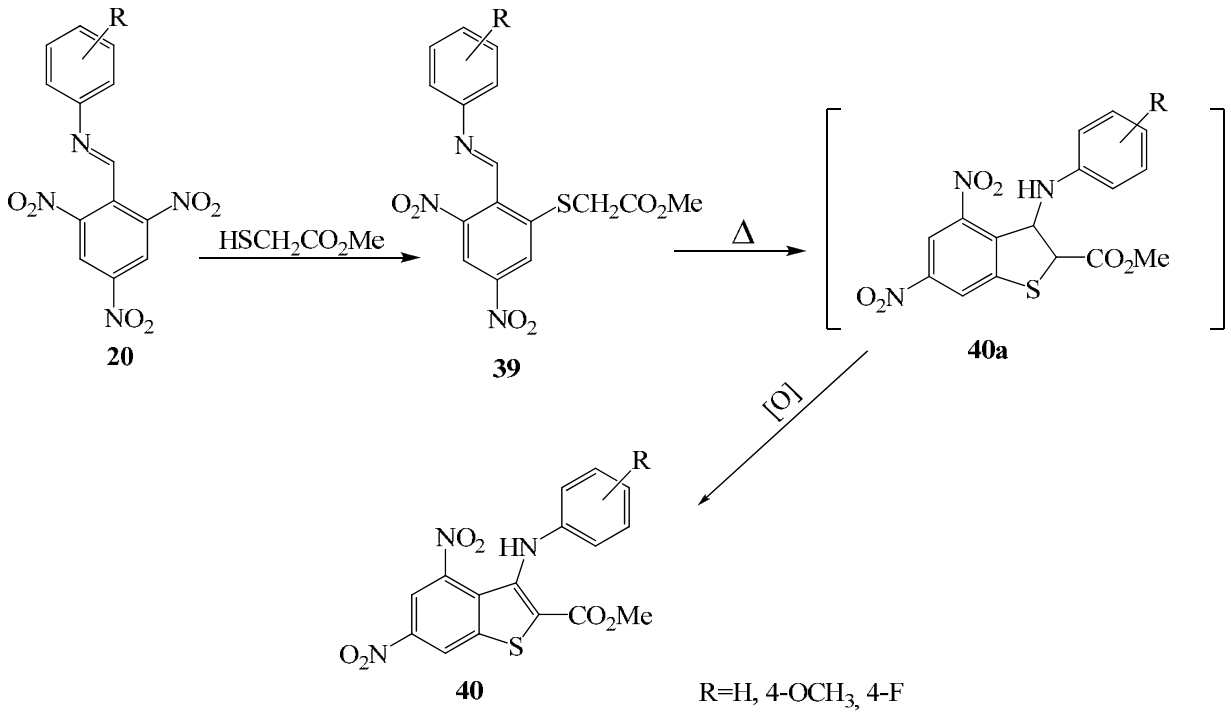


R= $PhCH_2$, $PhCH_2CH_2$, Me

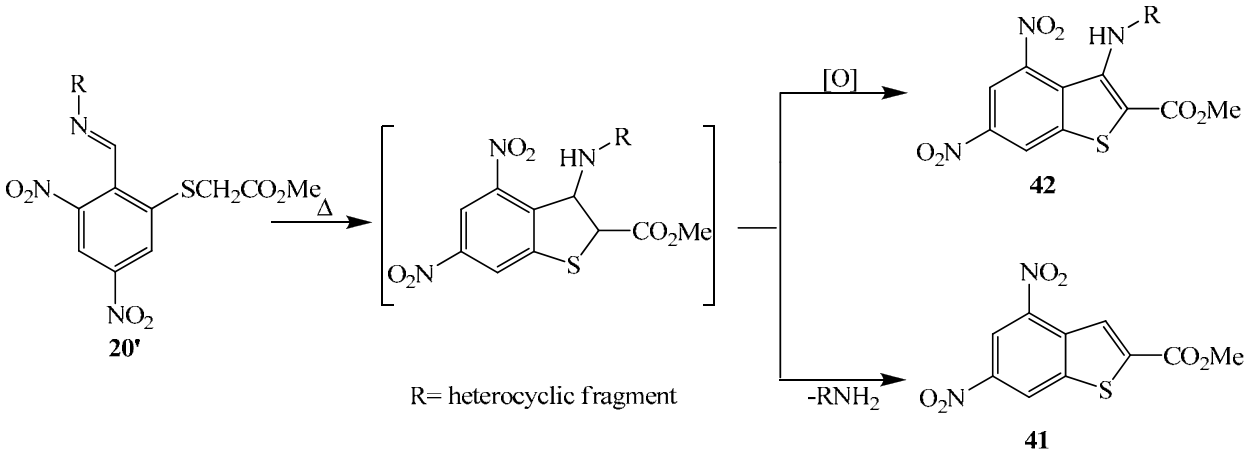
An interaction of trinitrobenzene with phenylacetamidines leads to 4,6-dinitroindole derivatives **38** in low yields.[58] In the authors' opinion, the indole formation is preceded by nucleophilic substitution of hydrogen in TNB, and then intramolecular substitution of the *ortho*-nitro group occurs.



A reaction of *N*-arylazometins **20** with the methyl ester of thioglycolic acid in the presence of K_2CO_3 in acetonitrile at room temperature leads to the *ortho*-nitro group substitution and formation of sulfides **39**. If the reaction is carried out in boiling acetonitrile, sulfides undergo intramolecular cyclization resulting in 3-arylamino-4,6-dinitrobenzo[*b*]thiophene-2-methylcarboxylates **40**.[59]

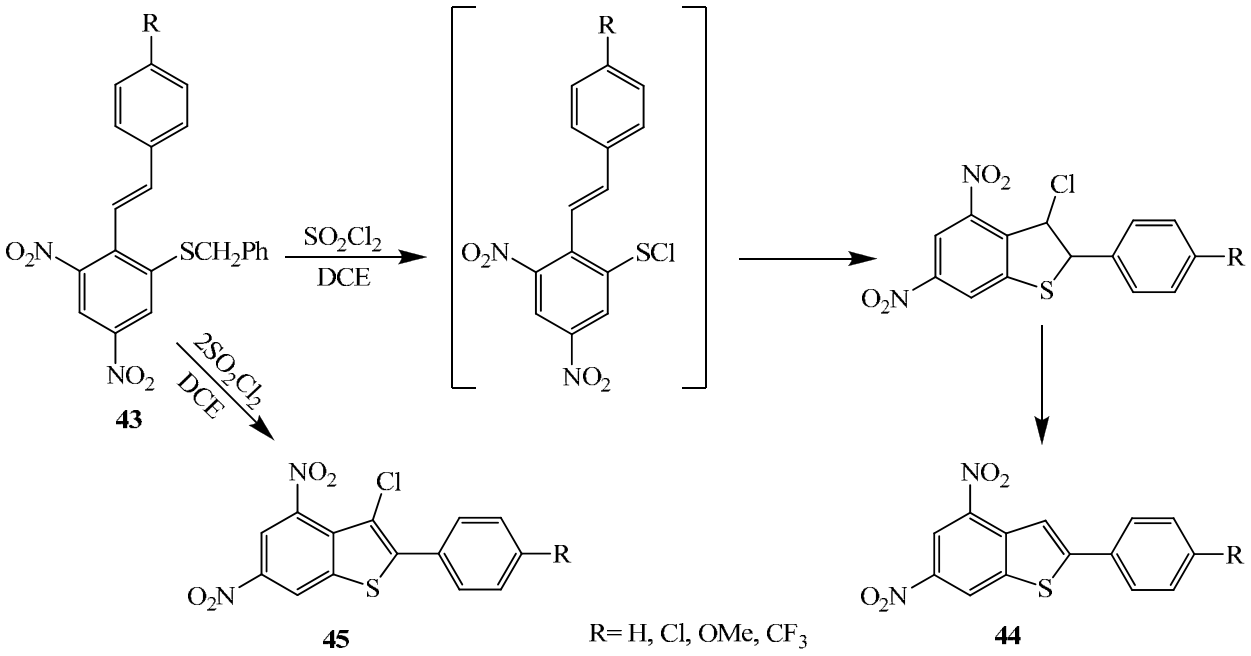


Of interest is that the main cyclization product of azometins **20'** is 4,6-dinitrobenzo[*b*]-thiophene-2-methylcarboxylate **41**, which is attained in a 40% yield as a result of the heterocyclic fragment elimination. Expected methyl 3-R-amino-4,6-dinitrobenzo[*b*]-thiophene-2-carboxylate **42** is produced in minor quantities (7% yield) as a reaction by-product.[59]

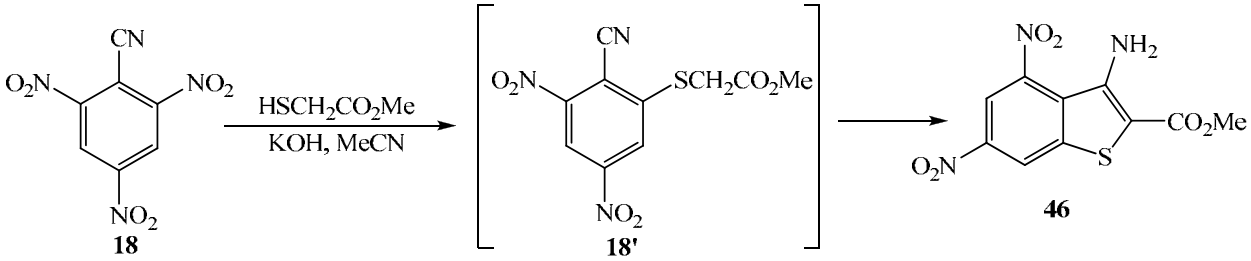


4,6-Dinitrobenzothiophenes can also be sourced from stilbenes **43** where the nitro group is substituted under the action of benzylmercaptan, and the substitution products cyclize to corresponding benzothiophenes under the action of sulfuryl chloride.[60,61] The $PhCH_2$-SAr bond is broken under the action of the chlorinating agent to yield corresponding arylsulfenyl chlorides capable of intramolecular cyclization. If an equimolar amount of sulfuryl chloride is used,

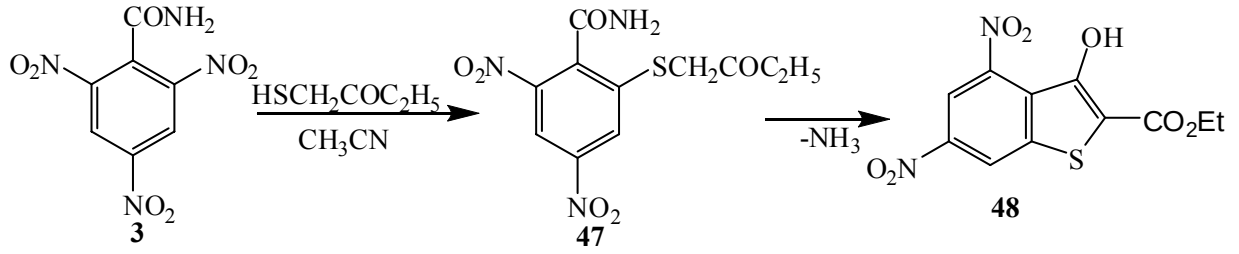
intermediates **44** are formed. It is curious that the interaction of sulfides **43** with excess of SO_2Cl_2 leads to 3-chlorobenzothiophenes **45**.



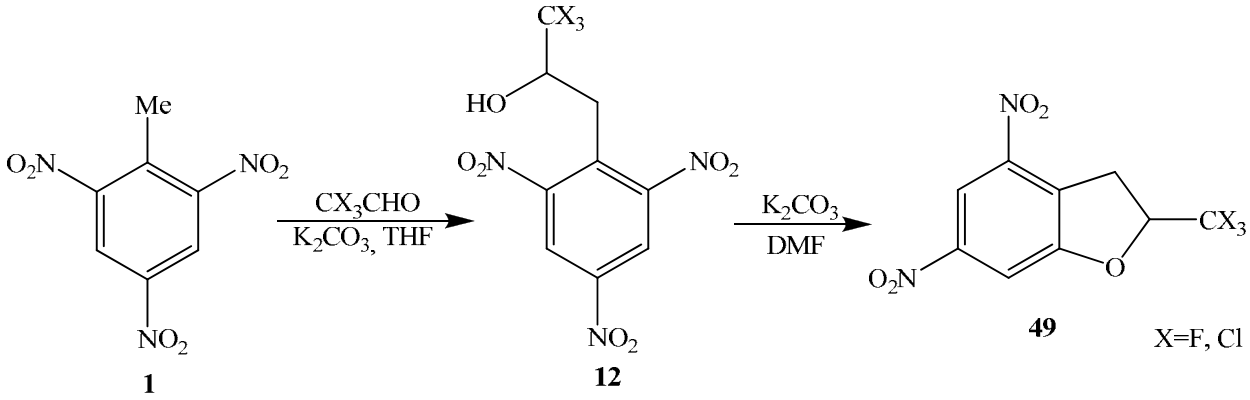
Benzothiophene derivatives can also be prepared on the basis of another TNT derivative - trinitrobenzonitrile **18**.[62] The *ortho*-nitro group in this compound is substituted selectively under the action of the thioglycolic ester. In the reaction conditions, sulfide **18'** undergoes intramolecular cyclization resulting in 3-aminobenzothiophene **46**. The product yield in this case is 50%. The authors of the other paper[63] isolated sulfide **18'** and exposed it to the MeONa action in methanol. In these conditions, the yield of compound **46** appeared to be higher (80%).



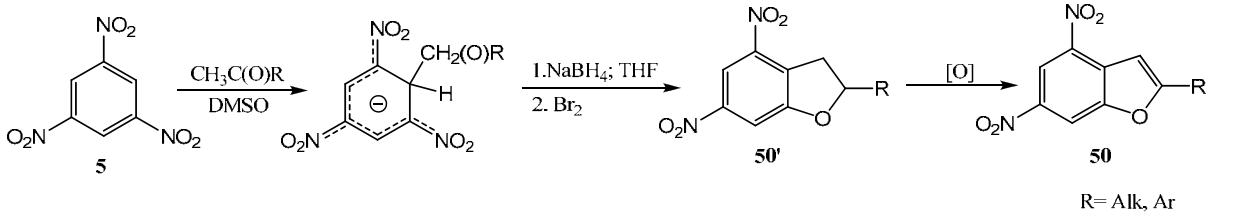
Trinitrobenzamide **3** has also been employed in the synthesis of benzannelated heterocycles.[64] Once amide **3** is affected by the ethyl ester of thioglycolic acid, *ortho*-nitro group substitution and subsequent intramolecular cyclization of sulfide **47** occur to yield 3-hydroxybenzothiophene **48**.



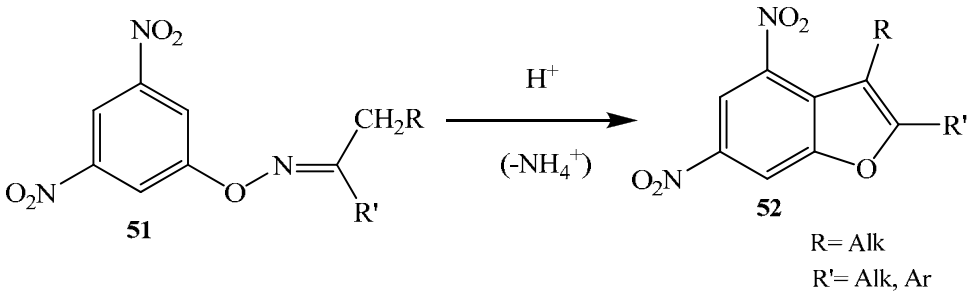
Alcohols **12** prepared by TNT condensation with fluoral and chloral under the action of a base are capable of intramolecular cyclization resulting in dihydrobenzofurans **49**.[22]



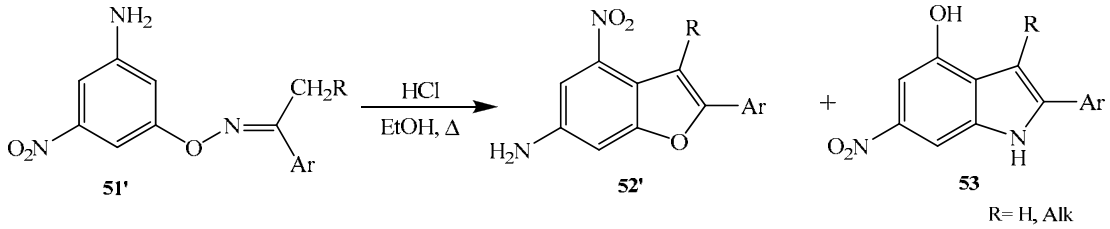
A TNB-based synthesis of 2-substituted 4,6-dinitro-2,3-dihydrobenzofurans has also been described.[9] TNB forms anionic adducts with acetone and acetophenone. Their reduction leads to intramolecular cyclization to give 2-substituted 4,6-dinitro-2,3-dihydrobenzofurans **50'**. The latter are dehydrogenated in pyridine to yield 2-substituted 4,6-dinitrobenzofurans **50**.



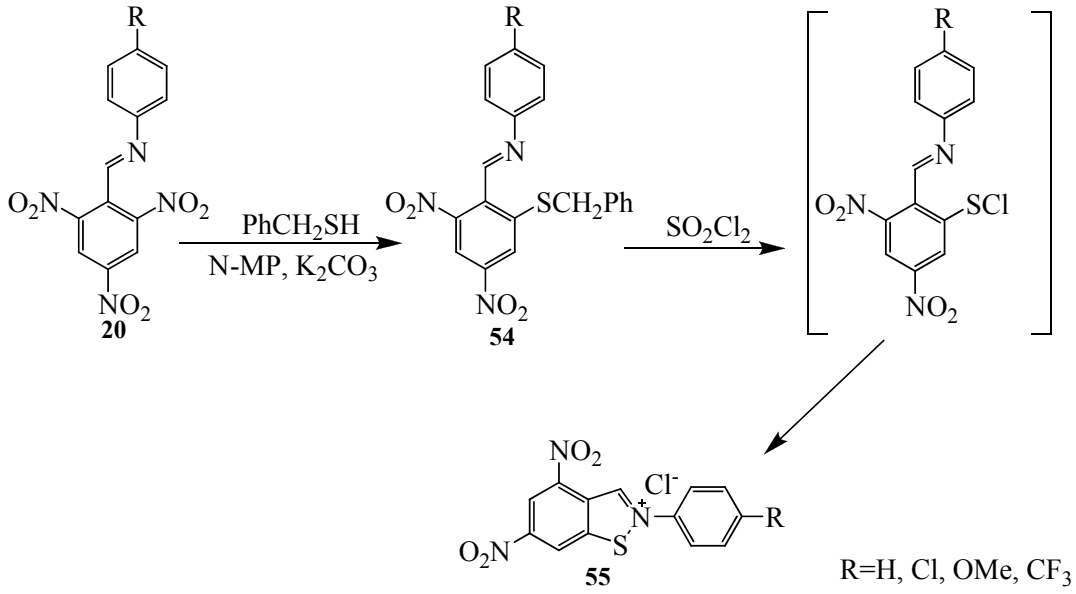
The ability of trinitrobenzene to substitute its nitro groups under the action of S-, N- and O-nucleophiles (such as aryl- and alkylketoximes) is well known. *O*-(3,5-Dinitrophenyl)ketoximes **51** cyclize smoothly yielding 4,6-dinitrobenzofurans **52** substituted in positions 2 and 3.[10] Cyclization proceeds in the acidic catalysis conditions: heating in HCl and CH_3COOH or H_2SO_4 and CH_3COOH mixtures.



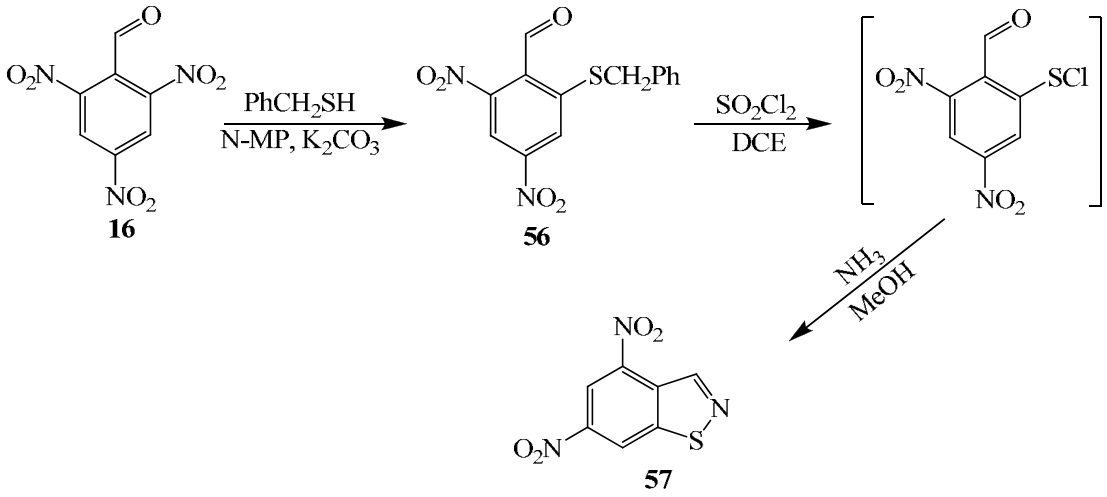
6-Amino-4-nitrobenzofurans and 4-hydroxy-6-nitroindoles are formed on heating of the products of selective reduction of oximes **51'** [*O*-(3-amino-5-nitrophenyl)ketoximes] in a mixture of conc. hydrochloric acid and ethanol.[11,12] The reaction product ratio is 1:1; they are separable due to different solubility in the reaction mixture.



2.3.2. Synthesis of benzannelated five-membered heterocycles with two heteroatoms. A synthesis of 4,6-dinitrobenzo[*d*]isothiazole derivatives was implemented using a strategy comprising the TNT methyl group transformation, regioselective *ortho*-nitro group substitution by an appropriate substituent, and cyclization of the synthesized derivative. Another paper describes a synthesis of 2-aryl-4,6-dinitrobenzo[*d*]isothiazolium chlorides.[65] These compounds are obtained through nucleophilic substitution of the *ortho*-nitro group in *N*-(2,4,6-trinitrobenzylidene)anilines under the action of benzylmercaptan and the reaction between sulfides **54** produced thereby and sulfonyl chloride in dichloroethane.

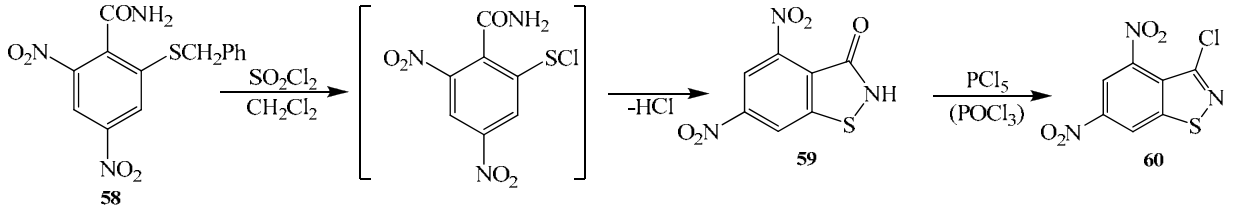


4,6-Dinitrobenzo[*d*]isothiazole was synthesized by a similar scheme.[66] In this case, a starting molecule was the 2,4,6-trinitrobenzaldehyde derivative obtained from *ortho*-nitro group substitution by benzyl mercaptan. A reaction of sulfide **56** with sulfuryl chloride in DCE leads to the S-CH_2Ph bond cleavage and formation of sulfenyl chloride, which, without additional purification, is introduced to a reaction with 20% ammonia solution in methanol. The only reaction product is 4,6-dinitrobenzo[*d*]isothiazole **57**.

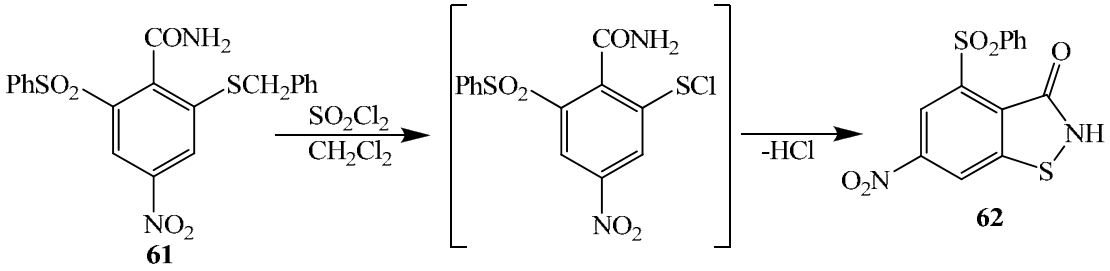


Ortho-substituted amides of 2,4,6-trinitrobenzoic acid are also of interest as potential synthons to achieve benzannelated five-membered heterocycles with two heteroatoms, e.g., the literature describes the preparation of 4,6-dinitrobenzo[*d*]isothiazolone derivatives from sulfide **58.**[64,67] Sulfenyl chloride is produced after treating compounds **58** with sulfuryl chloride, which

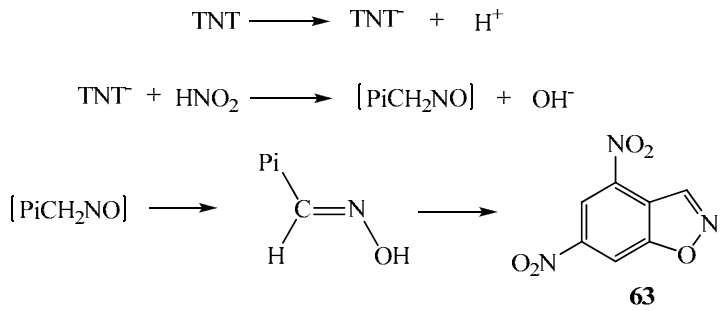
then spontaneously cyclizes to **59**. Compound **60** is generated upon the treatment of **59** with PCl_5 or $POCl_3$.



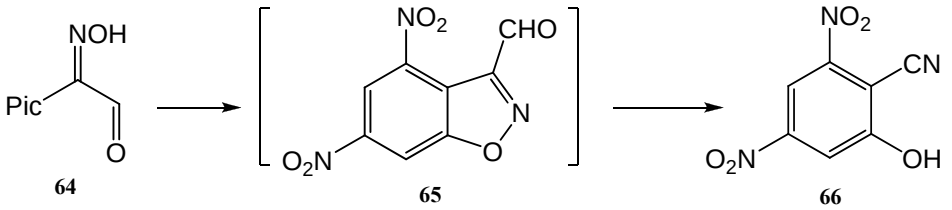
2-Benzylthio-4-nitrobenzamides containing other electron-withdrawing groups react in a similar manner, e.g., 2-benzylthio-6-benzylsulfonyl-4-nitrobenzamide **61** cyclizes readily to 4-benzylsulfonyl-6-nitrobenzo[*d*]isothiazol-3-one **62** (84% yield).[67]



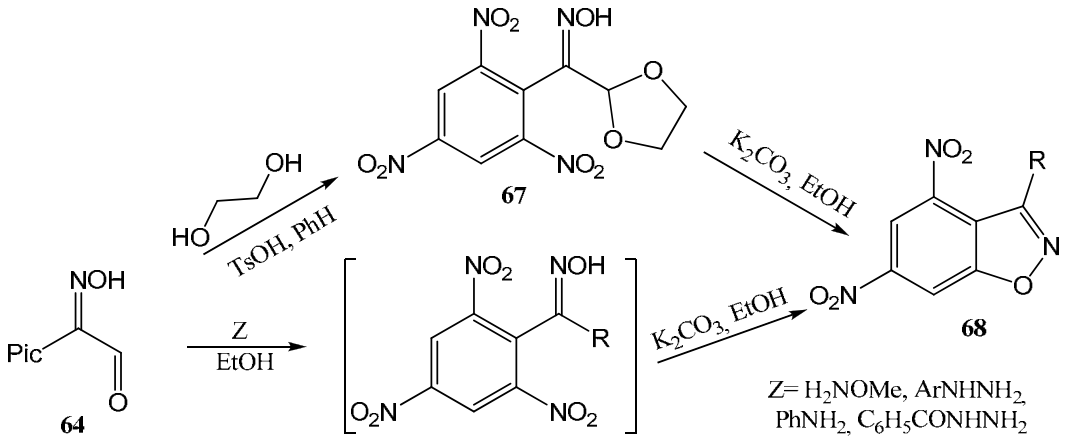
The literature provides data on TNT behaviour under photonitrosation conditions.[68] The photolysis of TNT water solutions with certain pH (a nitrite buffer) leads to the trinitrobenzyl anion leading to a number of products, among which 4,6-dinitrobenzo[*d*]isoxazole **63** was identified.



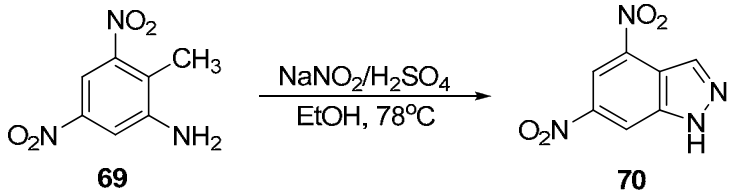
Nitrile of 4,6-dinitrosalicylic acid **66** is formed under the action of bases on 2-oxyimino-2-picrylacetaldehyde. Here the reaction is likely to proceed via a 4,6-dinitro-3-formylbenzo[*d*]isoxazole formation step with subsequent simultaneous decarbonylation and isoxazole cycle opening.[23,69]



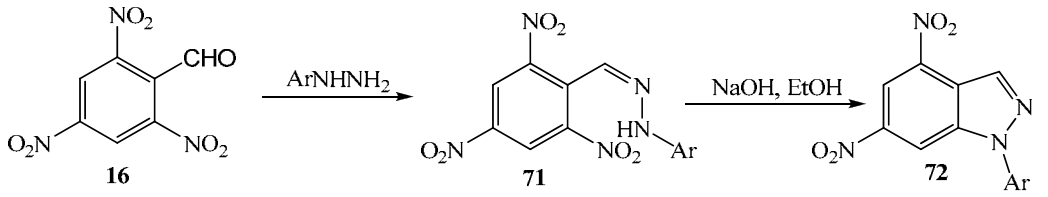
The formyl group protection in oxime **64** with the formation of respective acetal, hydrazones, *O*-methyloxime, and *N*-phenylamine allows implementing intramolecular nucleophilic substitution of the nitro group resulting in stable benzo[*d*]isoxazoles: 3-R-4,6-dinitrobenzo[*d*]isoxazoles **68** are formed on treatment of oximes **67** with K_2CO_3 in EtOH. Isoxazoles **68** can be prepared directly from oxime **64** without isolating the intermediates.[69]



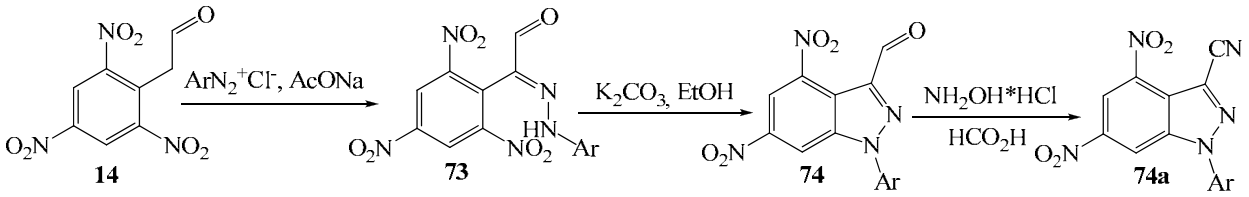
4,6-Dinitroindazole was prepared by diazotization of 2-amino-4,6-dinitrotoluene (a 2,4,6-trinitrotoluene partial reduction product).[70]



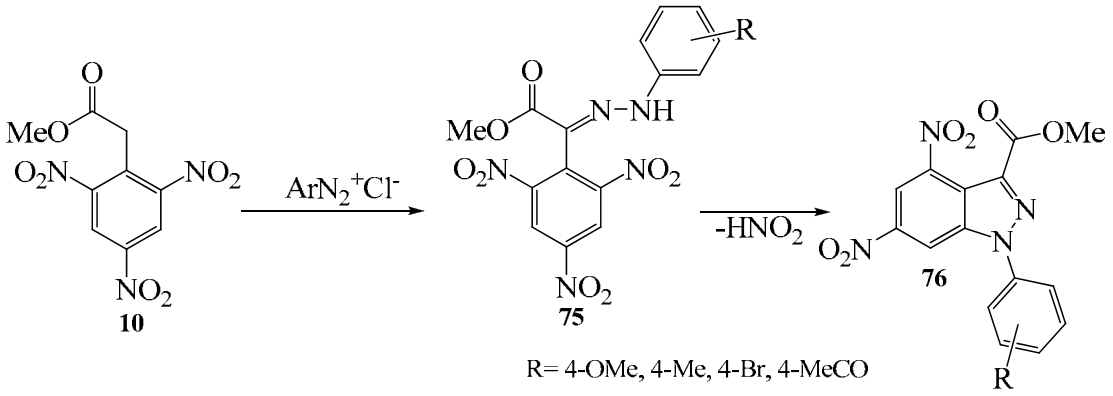
Along with 4,6-dinitroindazole (according to our data when this methodology is used the final product yield is ~ 50%), 2,4-dinitrotoluene, a diazonium salt reduction product, is attained.
A method for the synthesis of 1-aryl(hetaryl)-4,6-dinitro-1*H*-indazoles based on 2,4,6-trinitribenzaldehyde hydrazones is described.[26,71,72] Hydrazones **71**, in the presence of bases, undergo intramolecular cyclization accompanied by nucleophilic substitution of the *ortho*-nitro group, and indazoles **72** are produced.



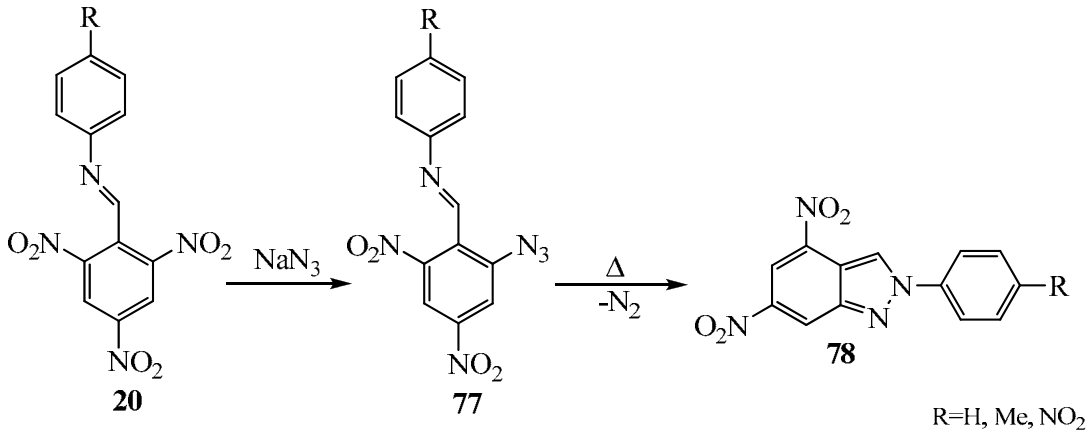
The azo-coupling products (picrylglyoxal monoarylhydrazones) are formed under the action of aryldiazolium salts on picrylacetaldehyde. When hydrazones **73** are treated with alkali or alkaline metal carbonates, 1-aryl-4,6-dinitro-3-formyl-1*H*-indazoles **74** are formed due to intramolecular substitution of the nitro group.[73,74] When **74** is treated with hydrochloric hydroxylamine in formic acid, nitrile **74a** is obtained.



The methyl ester of 2,4,6-trinitrophenylacetic acid reacts with diazonium salts in a similar way.[75] Hydrazones **75** undergo intramolecular cyclization to yield indazoles **76**.

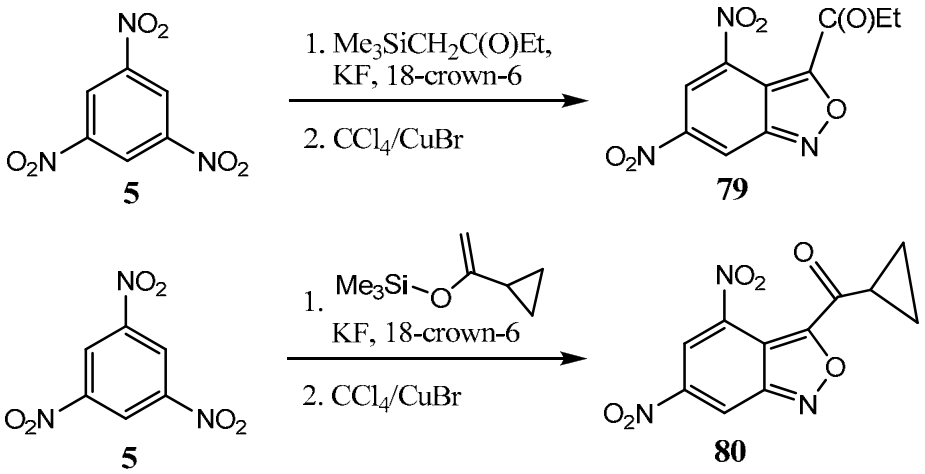


There are few publications regarding the synthesis of 2-substituted 4,6-dinitro-2*H*-indazoles.[28,32] These researches focus on imines prepared by trinitrobenzaldehyde condensation with aromatic amines. The *ortho*-nitro groups in compounds **20** are substituted selectively as affected by sodium azide. The thermolysis of azides **77** in ethylene glycol leads to indazoles **78**.



20 **77**

Meisenheimer complexes formed in TNB reactions with nucleophiles are able to react with the nitro groups present in the molecule under oxidation. In particular, examples of 4,6-dinitrobenzo[*c*]isoxazole formation on TNB interaction with organosilicon compounds in the presence of KF and 18-crown-6 with subsequent oxidation of CCl_4/CuBr are described.[76,77]



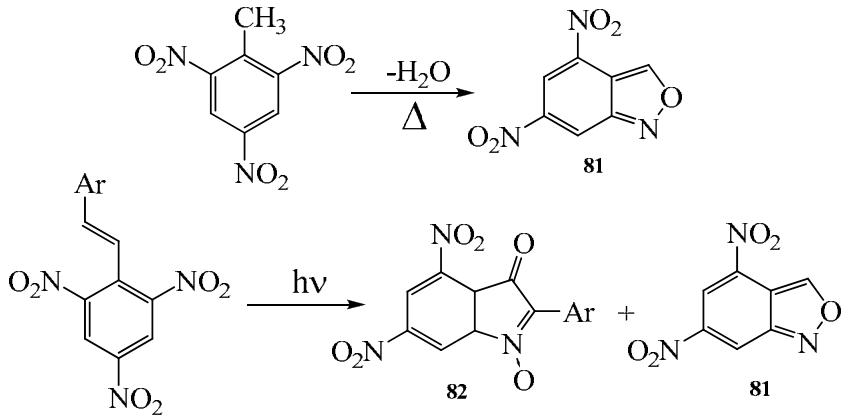
5 **79**

5 **80**

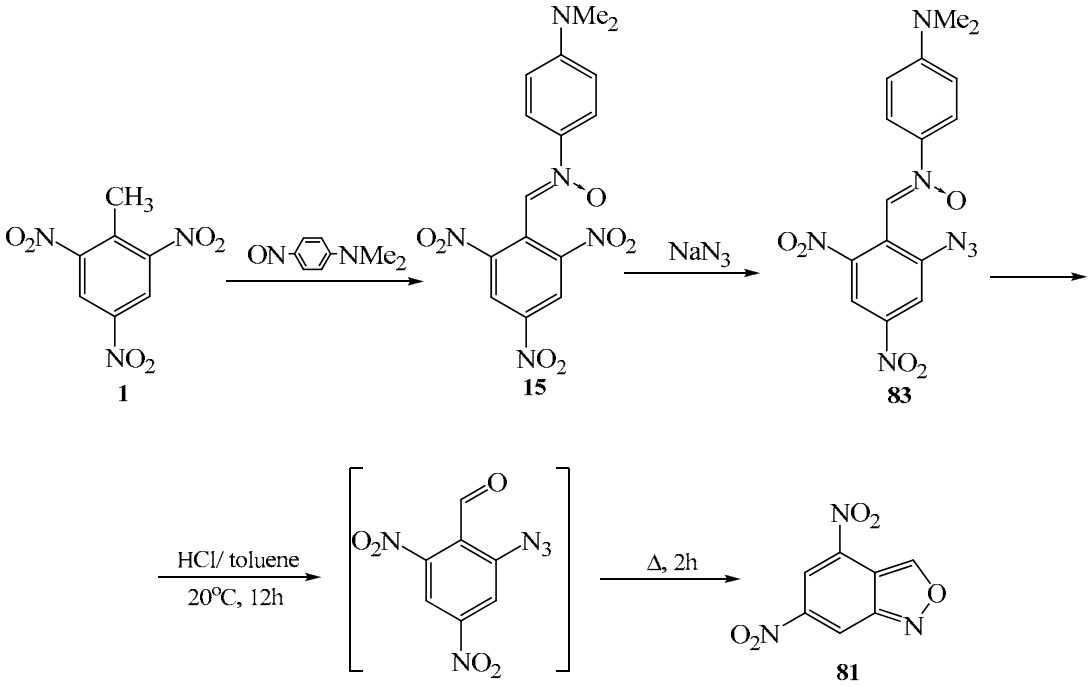
In addition, the literature cites data on the TNT-based preparation of one more representative of this class, i.e. 4,6-dinitrobenzo[*c*]isoxazole and its derivatives.[78-80] In particular, this compound was detected as a by-product in irradiation of 2,4,6-trinitrostilbenes **6.**[80] The main products of the stilbene photolysis are derivatives of isatogen **82**.

A synthesis of compound **81**, prepared in a low yield by the interaction of 2,4,6-trinitrobenzaldehyde with $TiCl_3$, has been reported.[80]

TNT thermal decomposition (during 16 h at 200^0C) has been discussed:[79,80] among the TNT thermolysis products, the authors isolated and identified 4,6-dinitroanthranyl **81** and its derivatives .



A preparative method for the synthesis of 4,6-dinitrobenzo[*c*]isoxazole has been developed recently.[81] As mentioned above, nitrone **15** in the reaction with NaN_3 gives azide **83**. Compound **83** upon heating under reflux in a toluene-HCl mixture leads to dinitroanthranyl **81**.



3. References

1. Castorina, T. C. In *Encyclopedia of explosives and related items*, Kaye, S. M., Ed., New Jersey: USA, 1980; Vol. 9, pp 235-298.

2. Zbarskii, V. L.; Zilin, V. F. Toluene and its nitro derivatives, Moscow: Editorial URSS, 1999, p 214 [in Russian].
3. Terrier, F. *Chem. Rev*. **1982**, *82*, 77
4. (a) Montagne, M. P. J. *Recl. Trav. Chim. Pays-Bas* **1902**, *21*, 384. (b) Jihane, A.; Mo, X.; Huimin, Z. *J. Am. Chem. Soc.* **2005**, *127***,** 5332. (c) Sachs, F.; Kempf, R. *Chem. Ber.* **1902**, *35*, 2712.
5. *Organic Synthesis, Coll.* Gilman, H., Ed.; Wiley: N.Y., 1946; Vol.1, p 541, p543.
6. Astrat'ev, A.; Marchukov, V.; Suschev, V.; Aleksandrov, A. *218th American Chemical Society National Meeting, Division of Organic Chemistry*, August 1999, Abstract No 50.
7. Zlotin, S. G.; Kislitsin, P. G.; Samet, A. V.; Serebryakov, E. A.; Konyushkin, L. D.; Semenov, V. V.; Buchanan III, A. C.; Gakh, A. A. *J. Org. Chem*. **2000**, *65*, 8430.
8. Severin, T.; Schmitz, R.; Temme, H-L. *Chem. Ber.* **1964**, *97*, 467.
9. Dutov, M. D.; Vatsadze, I. A.; Vorob'ev, S. S.; Shevelev, S. A. *Mendeleev Commun.* **2005**, 202.
10. Vorob'ev, S. S.; Dutov, M. D.; Vatsadze, I. A.; Kachala, V. V.; Strelenko, Y. A.; Sedov, A. V.; Shevelev, S. A. *Mendeleev Commun.* **2007**, 128.
11. Vorob'ev, S. S.; Dutov, M. D.; Vatsadze, I. A.; Petrosyan, E. P.; Kachala, V. V.; Strelenko, Yu. A.; Shevelev, S. A. *Russ. Chem. Bull. Int. Ed*. **2007**, *5*, 1020.
12. Secareanu, S. *Bull. Soc. Chim*. **1933**, *53*, 1395.
13. Lelievre, J.; Farrell, V; Terrier, F. *J. Chem. Soc., Perkin Trans II* **1986**, 333.
14. Pfeiffer, P.; Monath, J. *Chem. Ber*. **1906**, *39***,** 1304.
15. Ullmann, F.; Gschwind, M. *Chem. Ber*. **1908**, *41***,** 2291.
16. Pfeiffer, P. *Chem. Ber*. **1915**, *48***,** 1777.
17. Nisbet, H. B. *J. Chem. Soc.* **1927**, 2081.
18. Rozhkov, V. V.; Kuvshinov, A. M.; Gulevskaya, V. I.; Chervin, I. I.; Shevelev, S. A. *Synthesis* **1999**, *12*, 2065.
19. (a) Gilbert, E. E. *J. Energetic Mater.* **1984**, *2*, 215. (b) Bonecki, Z.; Urbanski, T. *Bull. Acad. Pol. Sci., Ser. Chim*. **1961**, *9***,** 463.
20. Barba, N. A.; Nedelko, M. S. *Zhurn. Organ. Khim.* **1983**, *19*, 1934.
21. Bonecki, Z.; Urbanski, T. *Bull. Acad. Pol. Sci., Ser. Chim*. **1961**, *9***,** 461.
22. Rozhkov, V. V.; Kuvshinov, A. M.; Shevelev, S. A. *Russ. Chem. Bull. Int. Ed*. **2000**, *3*, 573.
23. Vinogradov, V. M.; Dalinger, I. L.; Starosotnikov, A. M.; Shevelev, S. A. *Mendeleev Commun.* **2000**, 140.
24. Sachs, F.; Everding, W. *Chem. Ber*. **1903**, *36***,** 959.
25. (a) Secareanu, S. *Chem. Ber*. **1931**, *64***,** 834. (b) Secareanu, S. *Chem. Ber*. **1931**, *64***,** 836.
26. Starosotnikov, A. M.; Lobach, A. V.; Kachala, V. V.; Shevelev, S.A. *Russ. Chem. Bull. Int. Ed.* **2004**, *3*, 584.
27. Mezhnev, V. V.; Dutov, M. D.; Sapozhnikov, O. Yu.; Kachala, V. V.; Shevelev, S. A. *Mendeleev Commun.* **2007**, 234.

28. Kuvshinov, A. M.; Gulevskaya, V. I.; Rozhkov, V. V.; Shevelev, S. A. *Synthesis* **2000**, *10*, 1474.
29. Krohnke, F.; Borner, E. *Chem. Ber*. **1936**, *69***,** 2006.
30. Krohnke, F. *Chem. Ber*. **1938**, *71***,** 2583.
31. Tanasescu, I.; Nanu, I. *Chem. Ber*. **1939,** *72*, 1083.
32. Brovko, D. A.; Marshalkin, V. N.; Semenov, V. V. *Chem.Heterocycl. Comp*. **2001**, *4*, 504.
33. Sitzmann, M. E.; Dacons, J. C. *J. Org. Chem*. **1973**, *38*, 4363.
34. Guither, W. D.; Coburn, M. D.; Castle, R. N. *Heterocycles* **1979**, *12*, 745.
35. Buncel, M.; Crampton, M. R.; Strauss, M. J.; Terrier, F. Electron deficient aromatic- and heteroaromatic-base interactions. *The chemistry of anionic sigma complexes*, Elsevier: Amsterdam-Oxford-New York-Tokyo, 1984, p 273.
36. Shevelev, S. A.; Dutov, M. D.; Serushkina, O.V. *Russ. Chem. Bull. Int. Ed.* **1995**, *12*, 2424.
37. Serushkina, O. V.; Dutov, M. D.; Shevelev, S. A. *Russ. Chem. Bull. Int. Ed.* **2001**, *2*, 261.
38. Benedetti, F.; Marshall, D. R.; Stirling, C. J. M. *Chem. Commun.* **1982**, 918.
39. Shevelev, S. A.; Shakhnes, A. Kh.; Ugrak, B. I.; Vorob'ev, S. S. *Synth. Commun.* **2001**, *31*, 2557.
40. Kashaev, V. A.; Hisamutdinov, G. H.; Shevelev, S. A.; Valeshnii, S. I.; Shakhnes, A. Kh.; Bavrina, A. P. *Himicheskaya tekhnologiya* **2007**, *8*, 346 [in Russian].
41. Nielsen, T.; Henry, R. A.; Norris, W. P.; Atkins, R. L.; Moore, P. W.; Lepie, A. H. *J. Org. Chem*. **1979**, *44*, 2499.
42. Ruggli, P.; Zaeslin, H. *Helv. Chim. Acta* **1936**, *19*, 434.
43. Secareanu, S. *Bull. Soc. Chim. Fr.* **1932**, *51*, 591.
44. Secareanu, S.; Lupaş, I. *J. Prakt. Chem.* **1934**, *140*, 233.
45. Secareanu, S.; Lupaş, I. *J. Prakt. Chem.* **1934,** *140*, 90.
46. Secareanu, S. *Bull. Soc. Chim. Fr.* **1933,** *53*, 1017.
47. Chernyshev, V. V.; Yatsenko, A. V.; Kuvshinov, A. M.; Shevelev, S. A. *J. Appl. Cryst.* **2002**, *35*, 669.
48. Secareanu, S.; Lupaş, I. *Bull. Soc. Chim*. *Fr*. **1933**, *53*, 1436.
49. Secareanu, S.; Lupaş, I. *Bull. Soc. Chim*. *Fr*. **1934**, *1*, 373.
50. Secareanu, S.; Lupaş, I. *Bull. Soc. Chim*. *Fr*. **1935**, *2*, 69.
51. Mezhnev, V. V.; Dutov, M. D.; Shevelev, S. A. *Lett. Org. Chem*. **2008**, 5.
52. Rozhkov, V. V.; Kuvshinov, A. M.; Shevelev, S. A. *Synth. Commun.* **2002**, *32*, 1465.
53. Sapozhnikov, O. Yu.; Dyachuk, V. V.; Dutov, M. D.; Kachala, V. V.; Shevelev, S. A. *Russ. Chem. Bull. Int. Ed.* **2005**, *5*, 1331.
54. (a) Samet, A.V.; Zakharov, E. P.; Semenov, V. V.; Buchanan, A. C.; Gakh, A. A. *Synth. Commun.* **2001,** *31*, 1441. (b) Pullagurla, M.; Siripurapu, U.; Kolanos, R.; Bondarev, M. L.; Dukat, M.; Setola, V.; Roth, B. L.; Glennon, R. A. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 5298.
55. Rozhkov, V. V.; Kuvshinov, A. M.; Shevelev, S. A. *Org. Prep. Proced. Int.* **2000**, *32*, 94.
56. Eturi, S. R.; Bashir-Hashemi, A.; Iyer, S. U.S. Patent 5 969 155, 1999.

57. Sapozhnikov, O. Yu.; Mezhnev, V. V.; Dutov, M. D.; Shevelev, S. A. *Russ. Chem. Bull. Int. Ed.* **2005**, *4*, 1048.
58. Bard, R. R.; Strauss, M. I. *J.Org. Chem.* **1977**, *42*, 435.
59. Gulevskaya, V. I.; Kuvshinov, A. M.; Shevelev, S. A. *Heterocycl. Commun.* **2001** *7*, 283.
60. Sapozhnikov, O. Yu.; Mezhnev, V. V.; Dutov, M. D.; Kachala, V. V.; Shevelev, S. A. *Mendeleev Commun.* **2004**, 27.
61. Sapozhnikov, O. Yu.; Mezhnev, V. V.; Dutov, M. D.; Kachala, V. V.; Popov, N. A.; Shevelev, S. A. *Russ. Chem. Bull. Int. Ed.* **2005**, *3*, 711.
62. Dalinger, I. L.; Cherkasova, T. I.; Khutoretskii, V. M.; Shevelev, S. A. *Mendeleev Commun.* **2000**, 72.
63. Zlotin, S. G.; Kislitsin, P. G.; Kucherov, F. A.; Gakh, A. A. *Heterocycles* **2006**, *68*, 1109.
64. Shkinyova, T. K.; Dalinger, I. L.; Molotov, S. I.; Shevelev, S. A. *Tetrahedron Lett.* **2000**, *41*, 4973.
65. Sapozhnikov, O. Yu.; Mezhnev, V. V.; Smirnova, E. V.; Kimel, B. G.; Dutov, M. D.; Shevelev, S. A. *Mendeleev Commun.* **2004**, 207.
66. Sapozhnikov, O. Yu.; Smirnova, E. V.; Dutov, M. D.; Kachala, V. V.; Shevelev, S. A. *Mendeleev Commun.* **2005**, 200.
67. Zlotin, S. G.; Kislitsin, P. G.; Podgursky, A. I.; Samet, A. V.; Semenov, V. V.; Buchanan III, A. C.; Gakh, A. A. *J. Org. Chem*. **2000**, *65*, 8439.
68. Burlinson, N. E.; Sitzman, M. E.; Kaplan, L. A.; Kayser, E. *J. Org. Chem*. **1979**, *44*, 3695.
69. Vinogradov, V. M.; Dalinger, I. L.; Starosotnikov, A. M.; Shevelev, S. A. *Russ. Chem. Bull. Int. Ed.* **2001**, *3*, 464.
70. Brand, K.; Eisenmenger, Th. *J. Prakt. Chem.* **1913**, *87*, 487.
71. Reich, M. S. *Bull. Soc. Chim. Fr.* **1917**, 111.
72. Reddy, G. *Chem. Ind.* **1984**, *4*, 144.
73. Vinogradov, V. V.; Starosotnikov, A. M.; Shevelev, S. A. *Mendeleev Commun.* **2002**, 198.
74. Starosotnikov, A. M.; Kachala, V. V.; Lobach, A. V.; Vinogradov, V. M.; Shevelev, S. A. *Russ. Chem. Bull. Int. Ed.* **2003**, *8*, 1782.
75. Rozhkov, V. V.; Vorob'ev, S. S.; Lobach, A. V.; Kuvshinov, A. M.; Shevelev, S. A. *Synth. Commun.* **2002**, *32*, 467.
76. Kovalenko, S.V.; Artamkina, G. A.; Terent'ev, P. B.; Shevtsov, P. B.; Beletskaya, I. P.; Reutov, O. A. *Chem. Heterocycl.Compd*. **1990**, *3*, 357.
77. Kovalenko, S. V.; Artamkina, G. A.; Beletskaya, I. P.; Reutov, O. A. *Russ. Chem. Bull. Int. Ed.* **1987**, *12*, 2668.
78. Dacons, J. C.; Adolph, H. G.; Kamlet, M. J. *J. Phys. Chem.* **1970**, *74*, 3035.
79. Oxley, J. C.; Smith, J. L.; Ye, H.; McKenney, R. L.; Bolduc, P. R. *J. Phys. Chem.* **1970**, *99*, 9593.
80. Splitter, J. S.; Calvin, M. *J. Org. Chem*. **1955**, *20*, 1086.
81. Mezhnev, V. V.; Dutov, M. D.; Shevelev, S. A. *Mendeleev Commun*. In press.