



Preparation of Heat Resistant and Insensitive Explosives by Vicarious Nucleophilic Substitution (VNS) in Polinitroaromatic Compounds

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Abstract: Reaction of vicarious nucleophilic substitution (VNS) of hydrogen was applied for preparation of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) in a two-step process. Using this approach 3-amino-2,4,6,2'4'6'-hexanitrostilbene (MNHNS) and new 2,6-bis(3-amino-2,4,6-trinitrophenyl)-3,5-dinitropyridine (DAPYX) were obtained.

Keywords: DATB, HNS, PYX, amination, vicarious nucleophilic substitution, 3-amino-2,4,6,2'4'6'-hexanitrostilbene, 2,6-bis(3-amino-2,4,6-trinitrophenyl)-3,5-dinitropyridine

Introduction

It is well known, that the introduction of a picryl (2,4,6-trinitrophenyl) group into organic compounds enhances their explosive properties and thermostability. Heksanitrostilbene (HNS), 2,2',2'',4,4',4'',6,6',6''-nonanitroterphenyl (NONA) and 2,6-bis(picryl-amino)-3,5-dinitropyridine (PYX) are the proper examples.

Introduction of amino groups to the picryl rings in HNS yields the new compound that is more heat resistant. The same effect is observed in the case of 3,3'-diamino-2,2',4,4',6,6'-hexanitrodiphenylamine – a homologue of dipicrylamine

or 3,3'-diamino-2,2',4,4',6,6'-hexanitrodiphenyl ethylenediamine – a homologue of 2,2',4,4',6,6'-hexanitrodiphenyl ethylenediamine [1].

Some of described above aminopicryl derivatives are prepared by nucleophilic aromatic substitution of chlorine atoms in 1,3-dichloro-2,4,6-trinitrobenzene by the corresponding amines, then ammonia [1]. However, this method suffers from drawbacks, since 1,3-dichloro-2,4,6-trinitrobenzene is not easily available. Namely, its preparation requires nitration of 1,3-dichlorobenzene with mixtures of nitric acid and oleum at temperature above 100 °C, also amination occurs under elevated pressure and similar temperature conditions [2].

Alternative reaction used for introduction of various groups including amino one to nitroaromatic compounds is vicarious nucleophilic substitution (VNS) of hydrogen, discovered by Małkosza [3, 4]. Amination of aromatic nitro compounds by VNS can be carried out either by hydroxylamine [5, 6], 4-amino-1,2,4-triazol (ATA) [6, 7], 1,1,1-trimethylhydrazinium iodide (TMHI) [8] or sulfenamides [9] and a base. According to VNS reaction, electrophilic carbon atom in aromatic ring forms the σ^H complex with amine derivative. When an excess of a base is present, water in the case of hydroxylamine, 1,2,4-triazol in the case of ATA and hydrazine in the case of TMHI are eliminated from the corresponding σ^H complex. Finally, acidification of reaction mixture gives the product in which hydrogen atom is replaced by an amino group.

Due to above described restrictions connected with application of 1,3-dichloro-2,4,6-trinitrobenzene, amination of polynitroaromatic compounds by VNS reaction using hydroxylamine salts, TMHI or ATA seems easier and more effective way of preparation of new heat resistant explosives. Pagoria *et al.* [10] have already described successful preparations of explosives by VNS using these agents. They obtained 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) from 2,4,6-trinitroaniline (TNA), 3,5-diamino-2,4,6-trinitrotoluene (DATNT) from 2,4,6-trinitrotoluene and 4-amino-3,5-dinitropyrazole (LLM-116) from 3,5-dinitropyrazole. The LLM-116 example concerns amine derivative, which cannot be obtained by nucleophilic substitution of chlorine atom with ammonia, since the corresponding chloro derivative of 3,5-dinitropyrazole is not available [10].

In this work VNS reaction was applied for preparation of:

- TATB (looking for more effective route of its manufacture);
- not yet described amine derivatives of 2,6-bis(picrylamino)-3,5-dinitropyridyne (PYX);
- amine derivatives of HNS, not obtained by this method.

Results of these investigations are described below.

Results and discussion

In order to obtain above mentioned products, 2,4,6-trinitroaniline (TNA), heksanitrostilbene (HNS), and 2,6-bis(picrylamino)-3,5-dinitropyridine (PYX) were aminated applying VNS reaction.

In the case of TNA, hydroxylamine hydrochloride or ATA as aminating agents, and NaOH or various sodium alkoxides (methyl, ethyl, isopropyl, *tert*-butyl) in different ratios, and DMSO were used in order to obtain TATB. Preliminary experiments were carried out at ratio of TNA: aminating agent : base = 1 : 5-10 : 16-22, at temperatures ranging from ambient to 95 °C, and for 10.5 to 18 h, according to the literature data [11-13].

The use of hydroxylamine hydrochloride and sodium ethoxide gave a yellow-green solid. Values of elemental analysis calculated for neither 1,3-diamino-2,4,6-trinitrobenzene (DATB) nor TATB were correct. It seems that obtained product is not pure or underwent dehydration during heating. Aromatic compounds with adjoining amino and nitro groups undergo dehydration with formation of furazane structures, causing incorrect results of elemental analysis [2, 14].

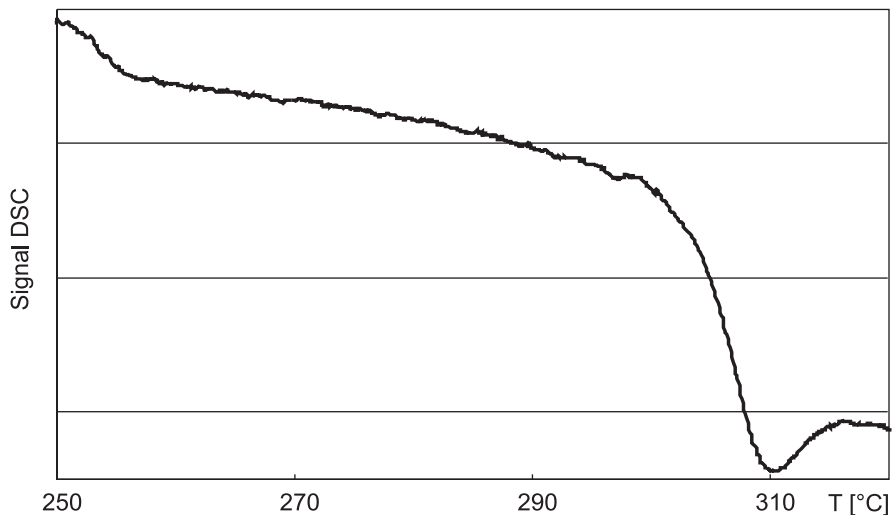


Figure 1. DSC of DATB obtained by amination of TNA with $\text{NH}_2\text{OH}\times\text{HCl}$.

DSC thermograph of the yellow-green solid does not show signal of melting but only wide signal of its decomposition at 310 °C (Figure 1). This thermograph is quite different comparing to that of TATB prepared by amination of 1,3,5-trichloro-2,4,6-trinitrobenzene with ammonia and shows a narrow signal at 375 °C originated from melting connected with decomposition [2]. The recorded thermograph is more similar to that of DATB obtained by amination of 1,3-dichloro-2,4,6 trinitrobenzene with ammonia, which shows a sharp signal at 286 °C of melting and a wide signal at 325 °C of decomposition (Figure 2).

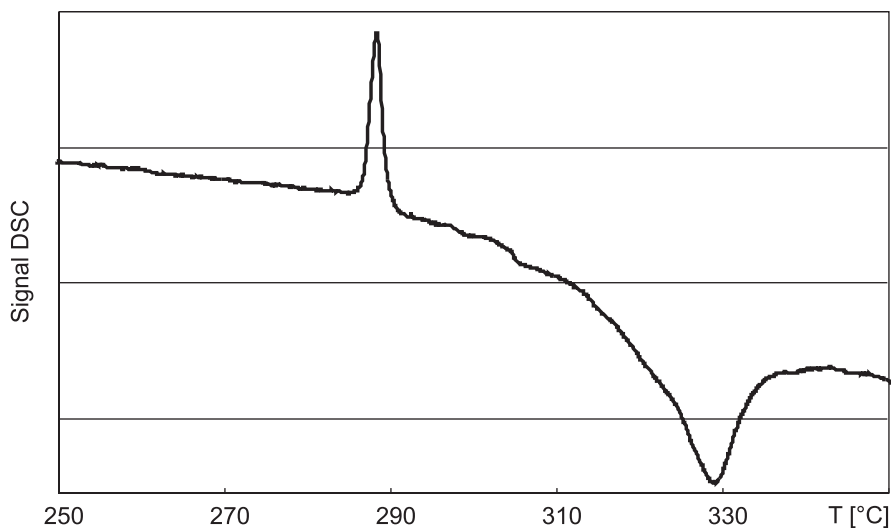


Figure 2. DSC of DATB obtained by amination of 1,3,5-trichloro-2,4,6-trinitrobenzene with ammonia.

Thus, it is assumed that the yellow-green solid is DATB contaminated with *e.g.* 1-amino-3-ethoxy-2,4,6-trinitrobenzene (product of substitution of amino by ethoxy group from sodium ethoxide). The substitution of amine by ethoxy group was observed when TATB was prepared *via* VNS reaction carried out in the presence of sodium ethoxide [2]. This impurity probably form eutectic with DATB, like ammonium diamide $[\text{NH}_4\text{N}(\text{NO}_2)_2]$ with ammonium nitrate which also does not exhibit melting point [15].

The highest yield (93%, assuming that the yellow-green product is pure DATB) was achieved when sodium ethoxide was used as base (TNA : $\text{NH}_2\text{OH}\times\text{HCl}$: EtONa = 1 : 5 : 16) and the reaction was carried out at ambient temperature for 10.5 h.

Amination of DATB with ATA occurred easily giving TATB [2], hence VNS reaction of the yellow-green solid was carried out under the same reaction conditions in order to obtain TATB. The following ratio of substrates was used: yellow-green solid (DATB) : ATA : MeONa = 1 : 5 : 10. The reaction was carried out for 21 h at ambient temperature giving TATB as yellow solid. DSC measurements indicated its melting point with decomposition at 365 °C and the same FT-IR spectrum like pure sample of TATB. The yellow solid shows the following bands which are assigned to amino and nitro groups (Figure 3):

- NH_2 (3320 and 3220 cm^{-1} : N-H asym. and sym., stretching vibrations; 1600 cm^{-1} : N-H def.; 1233 cm^{-1} : C-N – stretching vibrations);
- $\text{NO}_{2(\text{arom.})}$ (1566 and 1170 cm^{-1} : N-O asym. and sym., stretching vibrations; 860-760 cm^{-1} : C-N, stretching vibrations) [16].

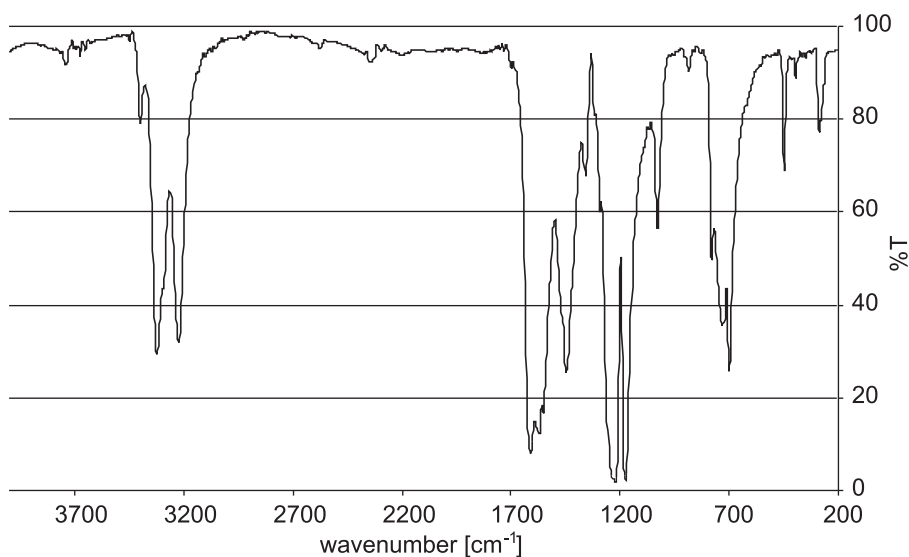


Figure 3. IR spectrum of TATB.

Absence of the bands in the range of 3100-3000 cm^{-1} , confirms lack of aromatic hydrogen atoms in the product what means that all ring hydrogen atoms were substituted. The relative low wave numbers of the N-H stretching bands indicate strong hydrogen bonds between amine hydrogen atoms and the adjacent nitro groups [16]. Formation of these bonds is typical for aminonitroaromatic compounds and was already described for TATB [17, 18]. TATB was obtained in yield of 92%.

TATB prepared by direct amination of TNA with ATA exhibits signals of melting with decomposition at 353 °C [2]. Therefore, TATB obtained from the yellow-green solid, is more pure than TATB obtained by the direct amination of TNA (see below) but less pure than that obtained by amination of 1,3,5-trichloro-2,4,6-trinitrobenzene with ammonia which melts at 375 °C, as we mentioned above [2].

Direct amination of TNA with ATA to TATB, was carried out at various ratios of the substrates, at temperatures from ambient to 60 °C, for 2.5-24 h, using different bases. The highest yield (85%) of TATB was achieved when sodium methoxide was used, at ratio of TNA : ATA : MeONa ca. 1 : 10 : 50, after 19 h at ambient temperature. According to DSC measurements, the product obtained under these conditions melted at temperature 363 °C with decomposition.

Taking into account the amounts of the substrates and yields of the products, preparation of TATB is suggested *via* two-step process:

- amination of TNA with cheap hydroxylamine hydrochloride to DATB;
- amination of such obtained DATB with a small amount of expensive ATA (ATA : DATB = 5 : 1) in the presence of sodium methoxide (direct amination of TNA with ATA to TATB requires large amount of ATA (ATA : TNA = 50 : 1)).

These two methods described above: direct and two-step amination give comparable yield of TATB (*ca* 85%).

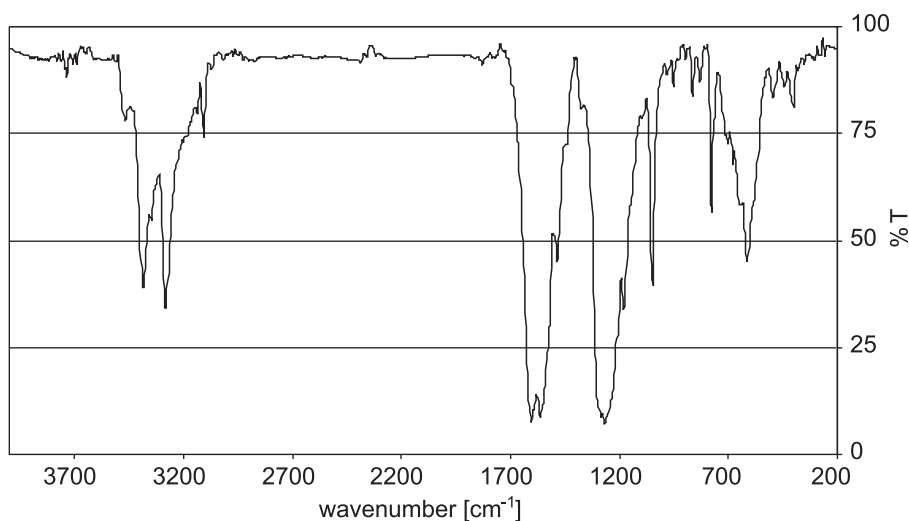


Figure 4. IR spectrum of DAPYX.

To check whether amination of HNS by VNS reaction is possible, it was allowed to react with hydroxylamine hydrochloride or ATA in the presence of various alkoxides.

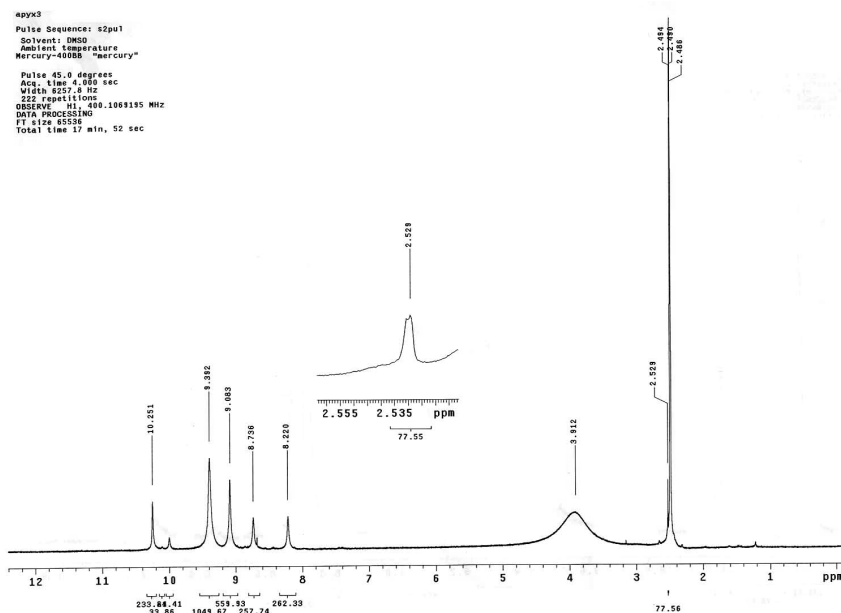


Figure 5. ^1H NMR of DAPYX.

In all cases crude red solids were obtained which decomposed at about 300 °C. All products were dissolved in sulfuric acid and after neutralization the red solids were recovered. Treated such a way, they decomposed at temperature 310 °C, it means at temperatures lower than pure HNS which melts at 315 °C [19]. Their elementary analyses gave values corresponding to monoaminated HNS – MAHNS, yield of this product varied from 52 to 71%.

Amination of PYX with hydroxylamine hydrochloride was unsuccessful leading only to decomposition of the substrate. When ATA was used, under the optimized conditions described above for amination of DATB, a brown product was obtained. It was dissolved in sulfuric acid and after neutralization brown solid was recovered. While heating, it decomposed rapidly at 200 °C, the temperature much lower than pure PYX, which melts with decomposition at 360 °C [1, 20].

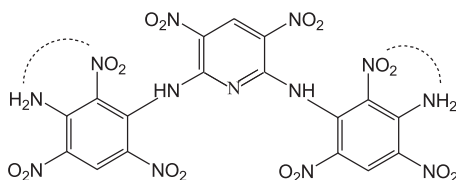
In IR spectrum of the brown solid (Figure 4), the following bands can be assigned to the amino, nitro groups and the C-H_{arom.} bonds:

- NH₂ (3384 and 3280 cm⁻¹: N-H asym. and sym., stretching vibrations; 1617 cm⁻¹: N-H def.; 1274 cm⁻¹: C-N – stretching vibrations);
- NO_{2(arom.)} (1544 and 1265 cm⁻¹: N-O asym. and sym., stretching vibrations; 589cm⁻¹: C-N, stretching vibrations);
- C-H_{arom} (3100 cm⁻¹: C-H stretching vibrations, 1019 cm⁻¹: C-H def. and 860 cm⁻¹ – band characteristic for 1,2,3,4,5-penta substituted benzene) [16].

This spectrum indicates that hydrogen atoms at C-3 and C-3' in picryl rings were replaced by amino groups. The bands of the picryl amino groups probably overlap with that of the 2,6-NH pyridine groups.

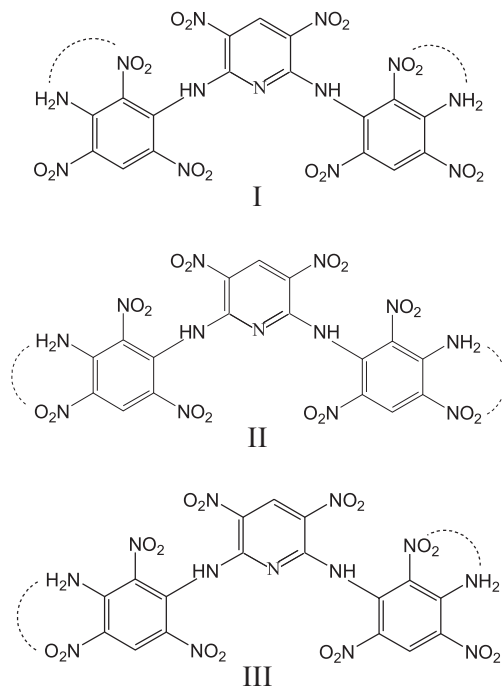
The ¹H NMR spectrum of the brown solid (Figure 5), apart from the signals of the product, exhibits the signals of DMSO at δ=2.5 ppm and water at δ=3.9 ppm. The signals at δ = 10.3 ppm [1H] and 9.1 ppm [2H] are assigned to the 4-pyridine proton and to the protons of 2,6-NH amino groups, respectively. Signals of similar chemical shifts were assigned to the same protons in the ¹H NMR spectrum of PYX [20]. The signals at δ = 8.2 ppm [1H] and at 8.7 ppm [1H] exhibited by the brown solid, can be assigned to the picryl protons, that at δ = 9.4 ppm [4H] to four protons of two NH₂ groups. The presence of amine groups in the brown solid was also confirmed by the IR spectrum.

Thus, the ¹H NMR and IR spectra indicate that two amine groups were incorporated to PYX molecule – each to the picryl ring. It allows us to propose the following structure of obtained brown solid – DAPYX:



DAPYX was obtained in yield of 90%.

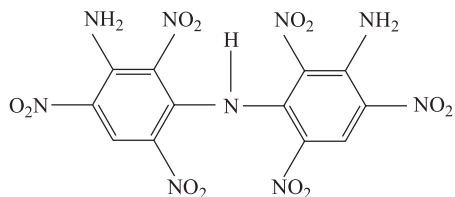
Two signals of protons in picryl rings in ¹H NMR spectrum of DAPYX indicate their magnetic nonequivalence. The amino and adjacent nitro groups in the picryl rings can form fairly stable intramolecular hydrogen bonds. If these bonds are formed only between *meta*-amino and *ortho*-nitro groups and between *meta*-amino and *para*-nitro groups with the same probability, the structures I, II and III are possible.



Scheme 1.

Integration of signals of picryl protons indicates equal population of the structures I and II or the structure III.

As was mentioned above, DAPYX obtained decomposed at 200 °C it means about 260 °C lower than the PYX. Usually, introduction of amino group(s) into polynitroaromatic compounds raises their melting point. But some aminonitrocompounds melt at lower temperature, *e.g.* 2,2',4,4',6,6'-hexanitrodiphenylamine melts at 241 °C [19], while 3,3'-diamino-2,2',4,4',6,6'-hexanitrodiphenylamine melts at 232-237 °C [1]. In DAPYX, formation of intramolecular hydrogen bonds between 2-nitro- and 3-amino groups in picryl rings is suggested (structures I and III). Such rigid structures may disturb interaction with bulky dinitropyridine substituent what causes that amino derivative melts at lower temperature than the parent nitro compound. A similar effect may probably acts in the case of 3,3'-diamino-2,2',4,4',6,6'-hexanitrodiphenylamine (structure IV) where interaction of two bulky picryl rings is disturbed by formation of intramolecular hydrogen bonds between 3-amino- and 2-nitro groups in these substituents. Consequently, amino derivative IV melts at lower temperatures than the corresponding nitro compound.



IV

Experimental

Solvents and reagents were of pure grade. DMSO was distilled under vacuum just before using. $\text{NH}_2\text{OH}\times\text{HCl}$ and $\text{NH}_2\text{OH}\times\text{H}_2\text{SO}_4$ (ZA Puławy) were used as received. CH_3ONa , $\text{C}_2\text{H}_5\text{ONa}$, $i\text{-C}_3\text{H}_7\text{ONa}$, $t\text{-C}_4\text{H}_9\text{ONa}$ were prepared from the corresponding alcohols and metallic sodium. 2,4,6-Trinitroaniline (TNA) and heksanitrostilbene (HNS) were prepared according to literature [14]. 2,6-bis(Picrylamino)-3,5-dinitropyridine (PYX) (Krupski Młyn) was used as received. 3-Amino-1,2,4-triazol was prepared according to [21]. 1,3-Diamino-2,4,6-trinitrobenzene (DATB) and 1,3,5-triamino-2,4,6-trinitrobenzene (standard samples) were kindly supplied by Institute of Industrial Organic Chemistry, Warsaw.

DSC measurements were carried out on a Pyris-Perkin-Elmer apparatus, IR spectra on Nicolet 60 SX0 and ^1H NMR spectra on Mercury – 400 BB spectrometer at 400 MHz in DMSO.

The synthesis described below were carried out according to the literature data [11-13].

Amination of TNA with $\text{NH}_2\text{OH}\times\text{HCl}$

To a flask equipped with magnetic stirrer 0.23 g (0.001 mole) of TNA, 0.35 g (0.005 mole) of $\text{NH}_2\text{OH}\times\text{HCl}$ and 10 cm^3 of dry DMSO were added. The orange solution was stirred and 0.8 g (0.016 mol) of MeONa was added. The mixture became black-marine and transparent. The reaction was carried out at 25 °C for 10.5 h. Then the mixture was poured into cold water (100 cm^3), the precipitated solid was filtered, washed several times with cold water and dried at 40 °C to give slightly impured DATB as yellow-green solid (yield 0.23 g, 93%).

Amination of TNA with ATA

Into a flask provided with a ground glass stopper and a magnetic stirrer 0.23 g (0.001 mole) of TNA, 0.84 g (0.01 mole) of ATA, 1.2 g (0.022 mole) of CH_3ONa

and 15 cm³ of DMSO were added during stirring. The reaction was carried out at 25 °C for 19 h. Then the mixture was poured into 3% aq. HCl (200 cm³), the yellow solid was filtered off, washed with water and dried at 40 °C to give TATB (yield 0.22 g, 85%).

Amination of DATB with ATA

Into a flask provided with a ground glass stopper and a magnetic stirrer 0.5 g (0.002 mole) of DATB, 0.86 g (0.01mole) of ATA and 15 cm³ of DMSO were added. The mixture was stirred till all reagents dissolved, then 1.12 g (0.012 mol) of CH₃ONa was added. The reaction was carried out for 21 h, poured into cold 5% aq. HCl (200 cm³), precipitated yellow solid was filtered off, washed several times with cold water and dried to give TATB (0.22 g, 93%).

Amination of HNS with NH₂OH×HCl

Into a flask equipped with a magnetic stirrer 0.45 g (0.001 mole) of HNS, 0.71 g (0.01 mole) of NH₂OH×HCl, 0.68 g (0.01 mol) of EtONa and 18 cm³ of dry DMSO were added. The mixture was stirred at ambient temperature for 5 h, poured into cold water (100 cm³), the precipitated red solid was filtered off, washed several times with cold water and dried at 40 °C to afford MAHNS (0.27 g, yield 54%). It melted at 300 °C with decomposition. The solid was dissolved in 15 cm³ of 96% H₂SO₄ and treated with 30% NaOH to pH = 10. The red solid was filtered, washed with water to pH = 7, it melted at 310 °C.

Amination of HNS with ATA

Into a flask provided with a ground glass stopper and a magnetic stirrer 0.45 g (0.001 mole) of HNS, 1.7 g (0.02 mole) of ATA and 18 cm³ of DMSO were added. The mixture was stirred till all reagents dissolved, then 2.2 g (0.04 mole) of CH₃ONa was added. The reaction was carried out for 18 h, poured into cold 5% aq. HCl (200 cm³), the red solid was filtered off, washed several times with cold water and dried to give MAHNS (yield 0.28 g, 59%). The solid was purified by dissolving in 96% H₂SO₄ and precipitated with 30% NaOH, as described above.

Elemental analysis: for 5-amino-2,2',4,4',6,6'-hexanitrostilbene (MAHNS), found C – 35.52%, H – 1.48%; N – 21.51%; calcd : C – 36.14%, H – 1.52%, N – 21.07%.

Amination of PYX with ATA

Into a flask provided with a ground glass stopper and a magnetic stirrer 0.31 g

(0.0005 mole) of PYX, 0.42 g (0.005 mole) of ATA and 15 cm³ of DMSO were added. The mixture was stirred and when all reagents dissolved 0.55 g (0.008 mole) of MeONa was added. The stirring was continued for 18 h, the mixture was poured to cold 3% aq. HCl (200 cm³), the brown solid was filtered, washed several times with cold water and dried giving 0.3 g of DAPYX (yield 92%). The product was purified as described above for MAHNS and analyzed by ¹H NMR and IR.

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