TECHNICAL TRANSACTIONS 2/2018
CHEMISTRY
DOI: 10.4467/2353737XCT.18.024.7997
SUBMISSION OF THE FINAL VERSION: 9/1/2018

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Chemistry of 2-aryl-1-cyano-1-nitroethenes. Part I. Synthesis and physical properties

Chemia 2-arylo-1-cyjano-1-nitroetenów. Część I. Otrzymywanie i właściwości fizyczne

Abstract

In this paper, we present the methodology of preparation of 2-aryl-1-cyano-1-nitroethenes and the synthesis of their main precursor – nitroacetonitrile. We have also gathered the physical properties of all compounds of this group known in the literature.

Keywords: 2-aryl-1-cyano-1-nitroethene, 3-aryl-2-nitro-2-propenenitrile, nitroacetonitrile, ACN, NAN, synthesis

Streszczenie

W niniejszej pracy przedstawiliśmy metodologię otrzymywania 2-arylo-1-cyjano-1-nitroetenów oraz ich głównego prekursora, jakim jest nitroacetonitryl. Przedstawiliśmy również właściwości fizyczne wszystkich znanych w literaturze związków ze wspomnianej grupy.

Słowa kluczowe: 2-arylo-1-cyjano-1-nitroeten, 3-arylo-2-nitro-2-propenonitryl, nitroacetonitryl, synteza

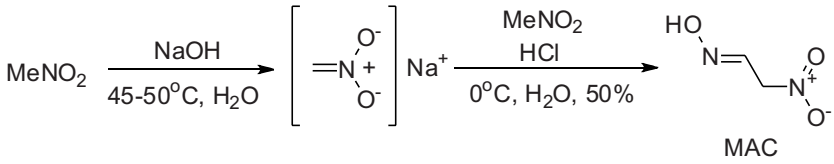
1. Introduction

Conjugated nitroalkenes (CNA) are highly effective synthons in organic synthesis. The presence of the nitro group in CNA molecule provides almost unlimited possibilities for its further functionalization towards, for example, carbonyl compounds (Nef reaction) [1–3], nitrile N-oxides (Mukuiyama reaction) [4], amino alcohols (via a Henry reaction/reduction sequence) [2, 5–7], salts and esters of nitronic acids [2, 4, 8] and many others [1, 2, 6, 9]. Additionally, due to their evidently electrophilic character, CNA are valuable reagents in cycloaddition processes leading to five- and six-membered cyclic systems [1, 10, 11].

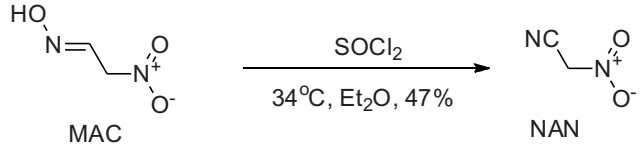
In this group of nitro compounds, 2-aryl-1-cyano-1-nitroethenes (ACN) are especially interesting. This type of CNA was first prepared in 1956 by Ried and Köhler [12]. Currently, more than 30 ACNs have been prepared and characterized. It is interesting that most experiments in this area have been performed recently. This confirms a growing interest in ACNs, and so we decide to review all physical and chemical aspects of the ACNs known. In the first part of our study, we characterized the synthetic protocols as well as the physical description of the compounds studied.

Preparation of nitroacetonitrile as a precursor for synthesis of ACNs

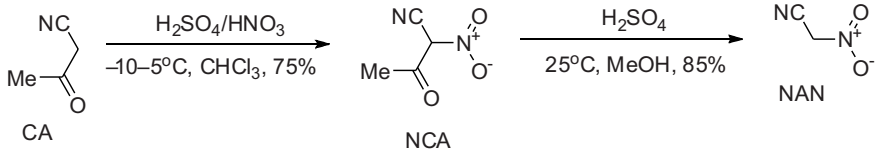
The methodology described in 1956 [12] for the preparation of nitroacetonitrile (NAN) is based on commercially available nitromethane [13, 14]. In the first step, nitromethane is converted into methazonic acid (MAC) via a condensation reaction catalyzed by NaOH, and in the next step acidification using concentrated HCl takes place. In this way methazonic acid can be prepared with a yield of 50% [14].



Dehydration of MAC leads to the formation of NAN. This process proceeds via a reaction involving thionyl chloride in a dry diethyl ether solution. Under these conditions, the final product may be synthesized with yields up to 47% [12, 14–18]. After purification using column chromatography (SiO_2/benzene) NAN of a purity suitable for use in Knoevenagel condensation is obtained. NAN is a pale yellow, unstable liquid, which at temperatures higher than 50–60°C is capable of exploding. Therefore, attempts to purify it via vapour distillation are potentially very dangerous [13].

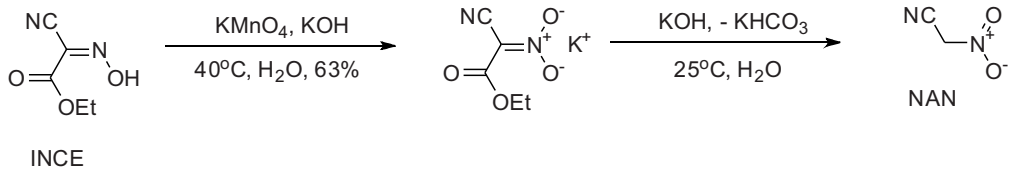


Kislyi and coworkers [19] have described an alternative, more effective synthetic way for preparing NAN. In this approach, NAN is synthesized according to a two-stage procedure: (i) nitration of cyanoacetone (CA) in a two-phase system, and next, (ii) deacylation of the nitrocarbonyl intermediate product (NCA).



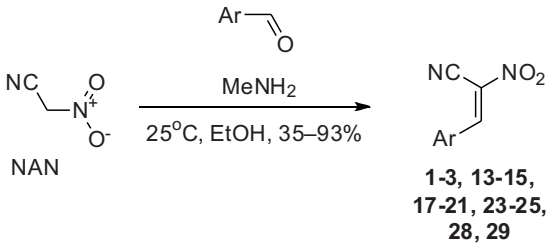
Unfortunately, no literature examples of a successful repeat of this procedure exist.

Very recently, a new procedure for NAN preparation was reported [20]. Based on ethyl ester of isonitrosocyanacetic acid (INCE), pure NAN was obtained with a moderate yield.

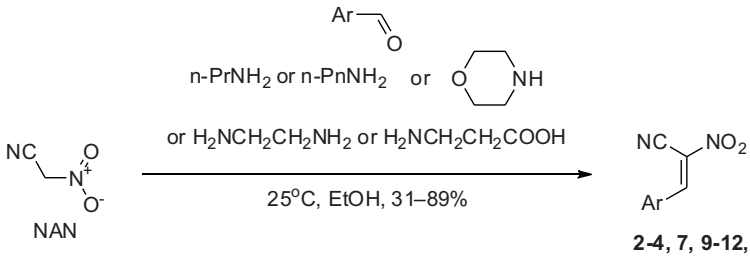


2. Preparation of ACNs

The first compounds in the ACN group were prepared by Ried and Köhler [12]. These authors described synthesis based on NAN and a series of aromatic aldehydes in the presence of a catalytic amount of methylamine generated *in situ*. This way, 11 new compounds (**1**, **3**, **13**, **17–21**, **24**, **28, 29**) were prepared with very different yields. An analogous methodology was also applied later in the case of ACNs **2**, **7**, **10**, **14**, **15**, **23** and **25** [21–24].

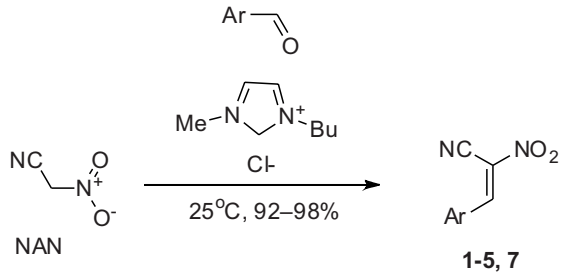


Later [18, 25–27, 28], other aliphatic and alicyclic amines (n-propylamine, n-pentylamine, morpholine, ethylenediamine, β-alanine) were also tested as catalysts in similar syntheses. In these syntheses several new compounds were prepared. It is interesting that these series contain many compounds (**2–4**, **9**, **11**, **12**, **16**) with electron-withdrawing groups (F, Br, COOMe) in aryl rings, which was not been prepared earlier.



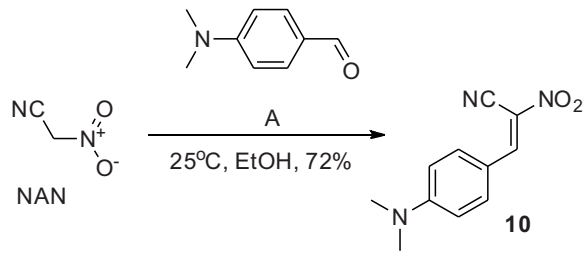
2-4, 7, 9-12, 14, 16, 24-27

In an alternative protocol, 1-butyl-3-methylimidazolium chloride has been used as a catalyst and as a reaction medium [17]. According to this procedure, six known earlier compounds (**1**–**5**, **7**) have been prepared with very high yields (>92%).



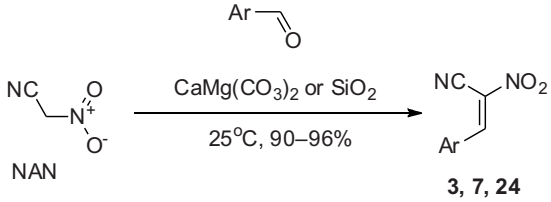
1-5, 7

For preparation of CNA **10** containing the EDG dimethylamino group in a phenyl ring, an alternative procedure using various acidic catalysts (A = $SOCl_2$, $AlCl_3$, 4-toluenesulphonic acid, HCl) was developed [29]. In particular, by this method compound **10** may be obtained with a yield up to 72%.



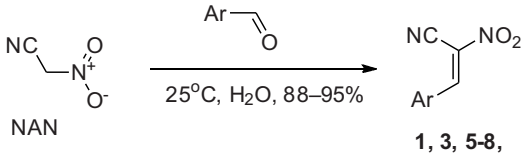
10

Heterogeneous catalysts have also been applied for the synthesis of ACNs. It was found that in the presence of dolomite $CaMg(CO_3)_2$ some aromatic aldehydes undergo condensation with the NAN yielding an expected CNA with a high yield [30]. In analogous processes, an SiO_2 catalyst was also applied [31].



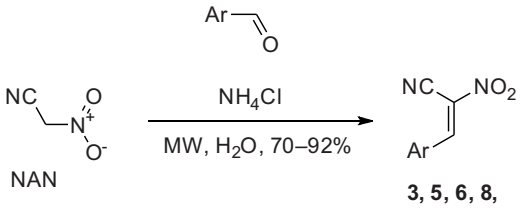
3, 7, 24

Recently, a "green" protocol for synthesis of series of ACNs has been described by Pizzo et al [32]. According to this procedure, 11 different compounds (**1**, **3**, **5–8**, **14**, **15**, **22**, **24**, **25**) were prepared in a water environment after 7h with high yields up to 95%.



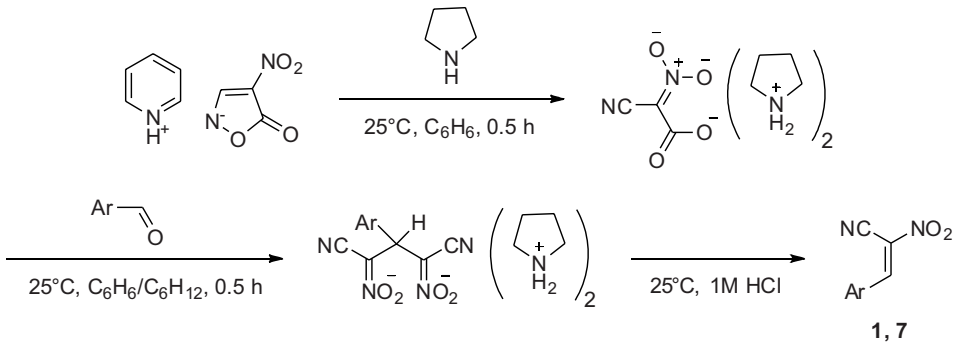
1, 3, 5-8, 14, 15, 22, 24, 25

Relatively faster than earlier methods are similar syntheses preformed in the presence of a catalytic amount of ammonium chloride [33]. Microwave irradiation of mixtures of NAN and appropriate aldehydes under these conditions give the expected products after 2–3 min(!).



3, 5, 6, 8, 14, 15

Independently of condensation between NAN and aromatic aldehydes, other strategies have been also tested for synthesis of ACNs. In particular, Blaha et al [34], analogously to earlier studies [35], analysed the possibility of preparing CNA **1** via chloronitration using nitryl chloride. Unfortunately, no attempts to obtain 1 were successful. On the other hand, Ariga et al [36] described an alternative synthetic pathway based on the pyridinium salt of 4-nitroisoxazolin-5(2H)-one. This way, the authors synthesized two ACNs (**1**, **7**) with almost quantitative yield. Unfortunately, at this time it is not known whether this is a universal method.



1, 7

Fundamental physical properties of all known ACNs are collected in Table 1.

3. Conclusion

The literature describes many methods for the preparation of conjugated nitroalkenes (CNA). Most universal strategies are based on the thermal or catalytic decomposition of nitroalkyl esters [37–41] and dehydrohalogenation of 1,2-dihalo-1-nitroethane derivatives [35, 42]. Unfortunately, all these protocols are inadequate for preparation of 2-aryl-1-cyano-1-nitroethenes. For this purpose only Knoevenagel condensation involving nitroacetonitrile is dedicated.

It should be mentioned at this point that most known ACNs were applied for synthesis of different type carbo- and heterocyclic compounds. These issues are the subject of the next part of our study.

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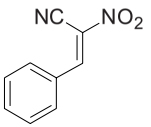
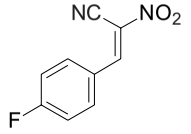
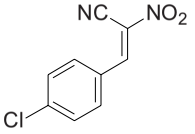
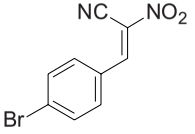
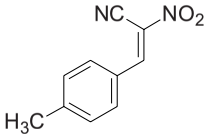
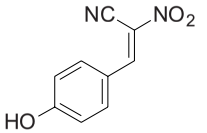
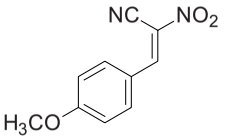
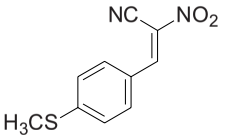
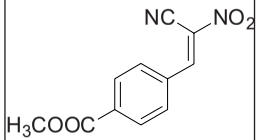
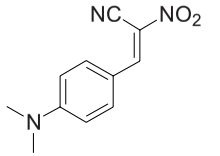
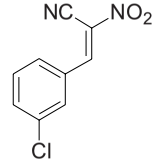
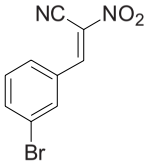
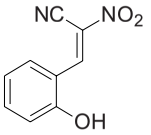
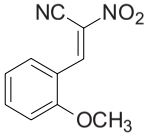
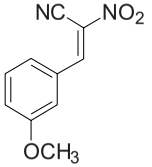
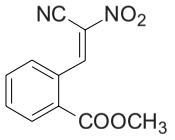
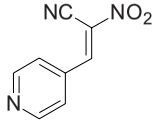
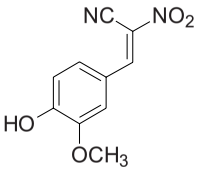
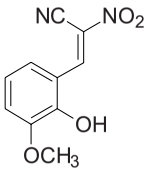
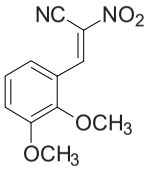
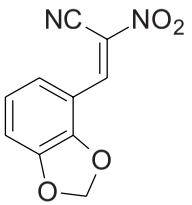
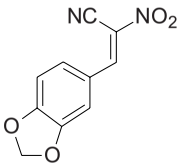
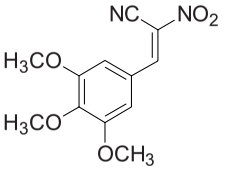
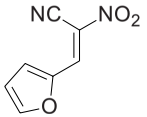
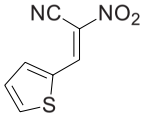
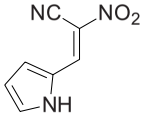
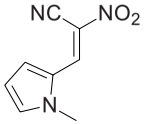
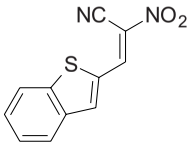
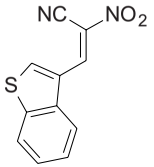
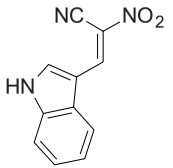
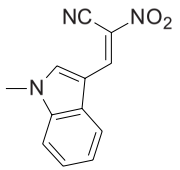
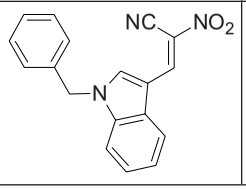
No.		t_t [°C] (solvent)	1H-NMR δ [ppm]	IR [cm^{-1}]	UV λ (log ε) [nm]	Ref.
1		102(EtOH) 101(CCl_4) 103-104($CHCl_3$)	9.01 (1H, s, CH) 8.11 (2H, m, 2CH) 7.60-7.74 (3H, m, 3CH) d_6-DMSO 8.66 (1H, s, CH) 8.01 (1H, dd, J_{23}=8.24, 2CH) 7.59 (1H, dd, J_{23}=8.24, 3CH) 7.69 (1H, tt, J_{24}=1.20 J_{34}=7.45, 4CH) $CDCl_3$	2229 (CN) 1615 (C=C) 1537 (NO_2) 1320 (NO_2)	328(4.23)	[12], [17], [18], [20], [23], [32], [34], [36]
2		116-117(EtOH)	8.65 (1H, s, CH) 7.19-8.18 (4H, m, Ar) $CDCl_3$	2231(CN) 1616(C=C) 1537(NO_2) 1327(NO_2)		[17], [18], [22], [25]
3		116-117(EtOH) 115-117(hex/AcOEt)	8.65 (1H, s, CH) 7.54-8.11 (4H, m, Ar) $CDCl_3$	2230(CN) 1615(C=C) 1548(NO_2) 1330(NO_2)		[12], [17], [18], [25], [30], [32], [33]
4		112-113(EtOH)	8.61 (1H, s, CH) 7.67-7.95 (4H, m, Ar) $CDCl_3$	2229(CN) 1620(C=C) 1538(NO_2) 1328(NO_2)		[17], [25]
5		93-94(EtOH) 94-96(hex/AcOEt)	8.63 (1H, s, CH) 7.92 (2H, d, J=8.80, 2CH) 7.40 (2H, d, J=8.80, 3CH) 2.51 (3H, s, CH_3) $CDCl_3$			[17], [32], [33]

No.		t_t [°C] (solvent)	1H-NMR δ [ppm]	IR [cm^{-1}]	UV λ (log ε) [nm]	Ref.
6		215-218(hex/AcOEt) 216-217(EtOH)	9.97 (1H, s, OH) 8.78 (1H, s, CH) 8.12 (2H, d, *J*=8.80, Ar) 7.11 (2H, d, *J*=8.80, Ar) d_6-acetone			[32], [33]
7		97-98(EtOH) 101(CCl_4) 104-105($CHCl_3$)	8.58 (1H, s, CH) 8.01 (2H, d, *J*=9.00, 2CH) 7.06 (2H, d, *J*=9.00, 2CH) 3.94 (3H, s, CH_3) $CDCl_3$	2229(CN) 1589(C=C) 1505(NO_2) 1317(NO_2)	382(4.48) CH_3CN 247(3.99) CH_3CN 367 MeOH 244 MeOH 390 EtOH	[12], [17], [18], [20], [23], [31], [32], [36]
8		115-117(hex/AcOEt) 117-118(EtOH)	8.55 (1H, s, CH) 7.90 (2H, d, *J*=8.80, Ar) 7.34 (1H, d, *J*=8.80, Ar) 2.55 (3H, s, CH_3) $CDCl_3$			[32], [33]
9		166-167(EtOH)	8.70 (1H, s, CH) 8.01-8.30 (4H, m, Ar) 3.99 (3H, s, CH_3) $CDCl_3$	2233(CN) 1624(C=C) 1542(NO_2) 1332(NO_2)		[18], [25]
10		189(EtOH) 182-183(C_6H_6)	8.49 (1H, s, CH) 7.93 (2H, d, *J*=8.50, 2CH) 6.76 (2H, d, *J*=9.50, 3CH) 3.20 (6H, s, $2CH_3$) $CDCl_3$	2213(CN) 1618(C=C) 1542(NO_2) 1389(NO_2)	485(4.67) 481(4.70)MeOH 275(3.90)MeOH	[18], [20], [23], [29]
11		67-68(EtOH)	8.60 (1H, s, CH) 7.42-8.02 (4H, m, Ar) $CDCl_3$	2235(CN) 1622(C=C) 1532(NO_2) 1334(NO_2)		[25]

12		85-86(EtOH)	8.59 (1H, s, CH) 7.37-8.09 (4H, m, Ar) $CDCl_3$	2233(CN) 1618(C=C) 1532(NO_2) 1331(NO_2)		[25]
13		136(CCl_4)				[12]
14		129-131(hex/AcOEt) 126(CCl_4) 130-132(EtOH)	9.21 (1H, s, CH) 6.97-8.31 (4H, m, Ar) 4.01 (3H, s, CH_3) $CDCl_3$	2235(CN) 1590(NO_2) 1330(NO_2)		[24], [32], [33]
15		118-120(hex/AcOEt) 118-119(CCl_4) 119-122(EtOH)	8.62 (1H, s, CH) 7.22-7.60 (4H, m, Ar) 3.88 (3H, s, CH_3) $CDCl_3$	2235(CN) 1590(NO_2) 1335(NO_2)	241 208	[24], [32], [33]
16		117-118(EtOH)	9.49 (1H, s, CH) 8.25-8.15 (1H, m, 3-H) 7.90-7.67 (3H, m, 4-H 5-H 6-H) 3.98 (3H, s, OMe) $CDCl_3$	2238 (CN) 1697 (COOMe) 1543 (NO_2)	303 (4.05) MeOH 223 (4.07) MeOH	[28]
17		100(CCl_4)				[12]

No.		t_t [°C] (solvent)	1H-NMR δ [ppm]	IR [cm^{-1}]	UV λ (log ε) [nm]	Ref.
18		168(CCl_4)	8.57 (1H, s, CH) 7.78 (1H, d, 2CH) 7.49 (1H, dd, 3CH) 7.08 (1H, d, 3CH) 6.50 (1H, s, OH) 4.01 (3H, s, CH_3) $CDCl_3$	2225(CN) 1620(C=C)	390(4.45)	[12], [23]
19		155-156(CCl_4)				[12]
20		101(CCl_4)				[12]
21		149(CH_3COOH)				[12]
22		142-143(EtOH)	8.56 (1H, s, CH) 6.94-7.70 (3H, m, Ar) 6.17 (2H, s, CH_2) $CDCl_3$			[32]

23		180(CCl_4)		2240(CN) 1570(NO_2) 1310(NO_2)		[21]
24		130(CCl_4) 126-127(EtOH)	8.43 (1H, s, CH) 7.93 (1H, d, J^3=1.55, CH) 7.54 (1H, d, J^3=3.43, CH) 6.81 (1H, dd, J^3=3.43, J^3=1.55, CH) $CDCl_3$	2234(CN) 1607(C=C) 1514(NO_2) 1307(NO_2)	371(4.33)EtOH	[12], [20], [23], [27], [30], [32]
25		168(EtOH)	8.81 (1H, s, CH) 8.04 (1H, d, J=4.91, CH) 8.00 (1H, d, J=4.02, CH) 7.36 (1H, dd, J=4.02, J=4.91, CH) $CDCl_3$	2225(CN) 1615(C=C)	375(4.25)EtOH	[20], [23], [27], [32]
26		174-175(EtOH)			420(4.67)EtOH	[27]
27		184-186(EtOH)			430(4.54)EtOH	[27]
28		194(CCl_4)				[12]

No.		t_t [°C] (solvent)	1H-NMR δ [ppm]	IR [cm^{-1}]	UV λ (log ε) [nm]	Ref.
29		203-204($CHCl_3$ or xylene)				[12]
30		215(CH_3NO_2)				[29]
31		207-208(CH_3NO_2)				[29]
32		211(CH_3NO_2)				[29]