

SHORT
COMMUNICATIONS

Dedicated to Prof. G.I. Koldobskii
on the 70th Anniversary of His Birth

Transalkenylation of Geminally Activated Nitroethenes

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Received March 14, 2003

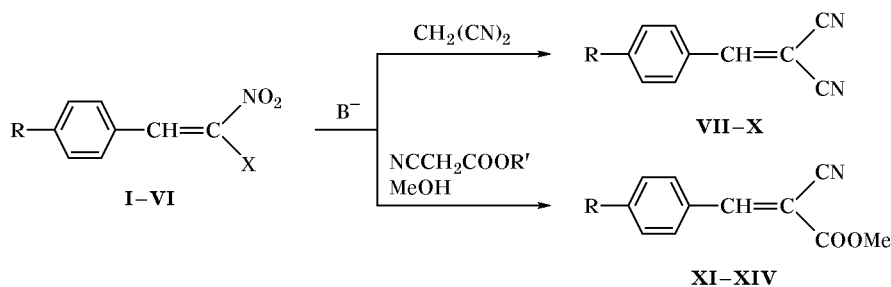
Geminally activated nitroethenes of the aromatic series, which contain a nitro or a carbonyl group as the second electron-acceptor function, are readily accessible compounds [1–4]. They exhibit high reactivity with respect to nucleophiles [2, 5–10]. Increased interest in the chemistry of such polyfunctional electron-deficient compounds is explained by the possibility for their ready modification via introduction of biologically active fragments (e.g., indole and substituted indole moieties [7, 8]), as well as for design on their base of new heterocyclic structures with useful properties (e.g., pyrazoles, 1,2,3-triazoles, etc. [9, 10]). Furthermore, a combination of two reaction centers in molecules of geminal acylnitroethenes, activated double bond and carbonyl group, makes them convenient models for studying regioselectivity problems in reactions with nucleophiles.

We have found that 2-aryl-1,1-dinitroethenes **I** and **II** and 2-aryl-1-acetyl(benzoyl)-1-nitroethenes **III–VI** readily react with CH acids having a cyano group, malononitrile and ethyl cyanoacetate, in alcoholic solution in the presence of a base (sodium methoxide,

triethylamine, or piperidine) to afford benzylidene-malononitriles **VII–X** and benzylidene-cyanoacetates **XI–XIV** (Scheme 1). The reaction with ethyl cyanoacetate in methanol using sodium methoxide as a base is accompanied by transesterification. The yield of compounds **VII–XIV** reaches 94%.

Presumably, CH acids having a cyano group react with nitroethenes **I–VI** at the double C=C bond, but the process does not stop at the stage of formation of addition product. In the presence of a base, elimination of dinitromethyl or acetyl(benzoyl)nitromethyl anion or so-called *arylmethylene transfer* [11] occurs. Our attempts to suppress the latter process and isolate primary nucleophilic addition products were unsuccessful. According to [11], exchange process in the transalkenylation reaction is governed by thermodynamic rather than kinetic factor. In fact, the efficiency of the reaction under study is determined primarily by thermodynamic stability of the resulting β,β -dicyano- and β -alkoxycarbonyl- β -cyanostyrenes. A significant role is likely to be played by the stability of the departing functionalized nitrocarbanion.

Scheme 1.



I, X = NO₂, R = H; **II**, X = NO₂, R = Cl; **III**, X = MeCO, R = Me₂N; **IV**, X = MeCO, R = MeO; **V**, X = PhCO, R = Me₂N; **VI**, X = PhCO, X = MeO; **VII**, **XI**, R = H; **VIII**, **XII**, R = Cl; **IX**, **XIII**, R = Me₂N; **X**, **XIV**, R = MeO; R' = Me, Et.

Rappoport and Ladkani [6] reported on a similar reaction of 1,1-dinitro-2,2-diphenylethene with malonodinitrile in the presence of triethylamine, which however required more severe conditions.

The structure of transalkenylation products **VII–XIV** was proved by independent synthesis from the corresponding aldehydes and cyano group-containing CH acids; no depression of the melting point was observed on mixing samples obtained by the two methods.

Thus, the reaction of β,β -dinitrostyrenes and β -acetyl(benzoyl)- β -nitrostyrenes with malononitrile and ethyl cyanoacetate takes the transalkenylation path and leads to formation of the corresponding benzyldenemalonodinitriles and benzyldenecyanoacetates.

Initial 2-aryl-1,1-dinitroethenes **I** and **II** [3, 4] and 2-aryl-1-acetyl(benzoyl)-1-nitroethenes **III–VI** [2, 12] were synthesized by known methods.

Benzyldenemalononitrile (VII). Three drops of triethylamine were added to a suspension of 0.194 g (1 mmol) of 1,1-dinitro-2-phenylethene (**I**) and 0.07 g (1 mmol) of malononitrile in 3 ml of anhydrous ethanol. The mixture was stirred for 1.5 h at room temperature and poured onto finely crushed ice containing acetic acid. The precipitate was filtered off. Yield 0.145 g (94%); light yellow crystals, mp 77–78°C (from ethanol); published data [13]: mp 83.5–84°C (from 2-methylbutan-2-ol).

4-Chlorobenzyldenemalononitrile (VIII) was synthesized in a similar way from 1,1-dinitro-2-(4-chlorophenyl)ethene (**II**) and malononitrile. Yield 33%, colorless crystals, mp 164–165°C (from ethanol); published data [14]: mp 162–163°C (from ethanol).

4-Dimethylaminobenzyldenemalononitrile (IX). Three drops of piperidine were added to a suspension of 0.23 g (1 mmol) of 4-(4-dimethylaminophenyl)-3-nitro-3-buten-2-one (**III**) and 0.07 g (1 mmol) of malononitrile in 3 ml of ethanol, and the mixture was left to stand for 1 h at room temperature. The precipitate was filtered off. Yield 0.16 g (83%), orange crystals, mp 173–174°C (from ethanol); published data [15a]: mp 179–180°C (from anhydrous ethanol).

Following an analogous procedure, compound **IX** was obtained from 3-(4-dimethylaminophenyl)-2-nitro-1-phenyl-2-propen-1-one (**V**) and malononitrile. Yield 83%, mp 173–174°C (from ethanol).

4-Methoxybenzyldenemalononitrile (X). A solution of sodium methoxide, prepared from 0.023 g (1 mmol) of metallic sodium and 2 ml of anhydrous methanol, was added to a suspension of 0.22 g

(1 mmol) of 4-(4-methoxyphenyl)-3-nitro-3-buten-2-one (**IV**) and 0.2 g (3 mmol) of malononitrile in 3 ml of anhydrous methanol. The mixture was heated to the boiling point and was then left to stand for 1 h at room temperature. The precipitate was filtered off. Yield 0.07 g (36%), yellow crystals, mp 107–108°C (from carbon tetrachloride); published data [15b]: mp 110°C (from ethanol).

Following an analogous procedure, compound **X** was obtained from 3-(4-methoxyphenyl)-2-nitro-1-phenyl-2-propen-1-one (**VI**) and malononitrile in the presence of piperidine. Reaction time 30 min; yield 70%, mp 107–108°C (from carbon tetrachloride).

Methyl 2-cyano-3-phenylpropenoate (XI). A solution of methyl cyanoacetate sodium salt, prepared from 0.1 ml (0.1 g, 1 mmol) of methyl cyanoacetate and 0.023 g (1 mmol) of metallic sodium in 5 ml of anhydrous methanol, was added dropwise at 0–3°C under continuous stirring to 0.194 g (1 mmol) of 1,1-dinitro-2-phenylethene (**I**). The mixture was stirred for 1 h at 0–3°C and for 4 h at room temperature and was poured onto finely crushed ice containing acetic acid. The precipitate was filtered off. Yield 0.123 g (66%), light yellow crystals, mp 86–87°C (from methanol); published data [16]: mp 88–89°C (from methanol).

Methyl 2-cyano-3-(4-chlorophenyl)propenoic acid (XII) was synthesized from 2-(4-chlorophenyl)-1,1-dinitroethene (**II**) and methyl cyanoacetate by the procedure described above for compound **XI**. Yield 90%, colorless crystals, mp 121–122°C (from ethanol); published data [17]: mp 121°C.

Methyl 2-cyano-3-(4-dimethylaminophenyl)propenoate (XIII) was synthesized from 4-(4-dimethylaminophenyl)-3-nitro-3-buten-2-one (**III**) and methyl cyanoacetate by the procedure described above for compound **XI**. Yield 53%, orange crystals, mp 134–135°C (from ethanol); published data [18]: mp 141–142°C (from ethanol).

Following an analogous procedure, compound **XIII** was obtained from 3-(4-dimethylaminophenyl)-2-nitro-1-phenyl-2-propen-1-one (**V**) and methyl cyanoacetate. Reaction time 12 h. Yield 30%, mp 134–135°C (from ethanol).

Methyl 2-cyano-3-(4-methoxyphenyl)propenoate (XIV) was synthesized from 4-(4-methoxyphenyl)-3-nitro-3-buten-2-one (**IV**) and ethyl cyanoacetate by the procedure described above for compound **XI**. Yield 80%, yellow crystals, mp 97–99°C (from ethanol); published data [18]: mp 100–101°C (from ethanol).

Following an analogous procedure, compound **XIV** was obtained from 3-(4-methoxyphenyl)-2-nitro-1-phenyl-2-propen-1-one (**VI**) and ethyl cyanoacetate. Yield 78%, mp 98–99°C (from ethanol).

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