

N,N-Dimethylformamide Dimethylacetal (DMF-DMA) Catalyzed Formation of 1,3,5-Trisubstituted Benzene Derivatives from α,β -Unsaturated Nitro Compounds

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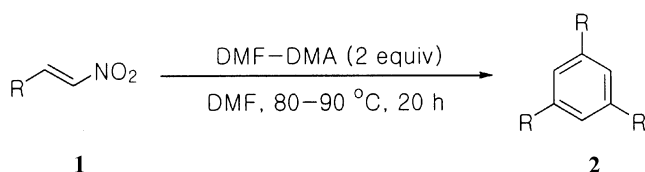
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N,N-Dimethylformamide dimethylacetal (DMF-DMA) has been used as a methylating agent of various compounds.¹ Recently, we have reported on the formation of *N*-methyl-*N*-tosyl allylic amine derivatives from the Baylis-Hillman adducts of *N*-tosylimines with the aid of DMF-DMA.² In the reaction, trace amounts of methoxide ion in DMF-DMA might trigger the whole reaction.² In order to find some useful applications of the catalytic activity of methoxide ion in DMF-DMA, we examined on the reaction of β -nitrostyrene³ and DMF-DMA in order to prepare 1,3,5-triarylbenzene derivatives, which are useful compounds in the fields of electrode and electroluminescent devices⁴ or in the chemistry of conducting polymers.⁵ Transition metal catalyzed [2+2+2] cycloaddition reaction of phenylacetylene derivatives to form 1,3,5-triarylbenzenes have been well studied.⁶ Recently, $\text{TiCl}_4(\text{OTf})$ catalyzed formation of 1,3,5-triarylbenzenes from acetophenone derivatives have been reported.⁷ There was a report on the formation of 1,3,5-triphenylbenzene (5%) in the course of reduction of β -nitrostyrene with *N*-benzyl-1,4-dihydronicotinamide.⁸

As expected we could obtain 1,3,5-triphenylbenzene (**2a**)⁷ in 34% isolated yield from the reaction of β -nitrostyrene (**1a**) and DMF-DMA (2 equiv) in DMF at 80–90 °C within 20 h as shown in Scheme 1. Some variations in reaction conditions such as temperature, amounts of DMF-DMA, or reaction time did not improve the yield of **2a**.

Substituted β -nitrostyrene derivatives **1b–c** or heterocyclic derivatives **1d–e** afforded the corresponding compounds **2b–e** in 20–40% yields. However, alkyl derivative **1f** or β -substituted nitro olefin **1g** did not give the desired products. The mechanism for the formation of 1,3,5-triarylbenzenes **2a–e** can be proposed as shown in Scheme 2. Addition of methoxide ion to β -nitrostyrene gave a new nucleophilic intermediate **I**, which adds to β -nitrostyrene to give **II**, same reaction once again, cyclization, elimination of nitrous acid afford the desired product.⁸

In the cases of **1h** and **1i**, which have strong electron withdrawing nitro substituent on the benzene ring, we could obtain methyl benzoate derivatives **3h** and **3i** in 15–22% yields instead of the expected cyclic trimerization products as shown in



Scheme 1

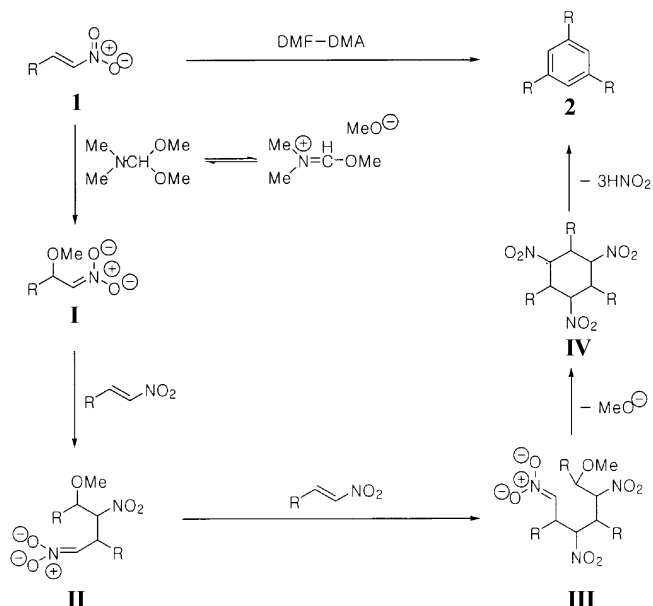
Table 1. The reaction mechanism for the formation of **3h** and **3i** is uncertain at this point.

In the reaction mixtures of **1a** and DMF-DMA, we could not detect phenylacetylene or acetophenone on tlc. Moreover, from the reaction of phenylacetylene or acetophenone and DMF-DMA in DMF we could not observe 1,3,5-triphenylbenzene.¹⁰ Thus the possibility of formation of the cyclic trimerization product **2** via phenylacetylene or acetophenone could be excluded completely.

The reaction was also effective with sodium methoxide (2 equiv, 28% methanol solution) in DMF. The use of DMF as solvent was found to be crucial. The same reaction of **1a** with sodium methoxide in methanol did not give **2a** in appreciable yield. The results might be due to the basic nature of DMF, which can trap the eliminated nitrous acid. Without DMF-DMA or sodium methoxide no reaction occurred. The reaction of **1a** with *N,N*-dimethylformamide diethylacetal gave **2a** in lower yield (10%).

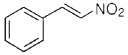
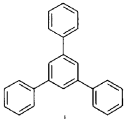
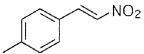
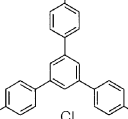
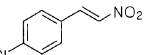
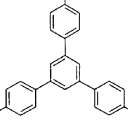
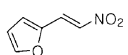
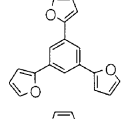
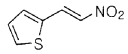
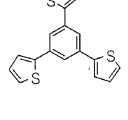
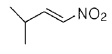
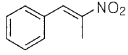
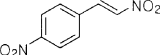
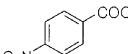
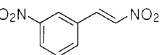
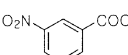
In this report we developed a simple preparation method of 1,3,5-triarylbenzene derivatives from the easily available β -nitrostyrene derivatives with the aid of methoxide ion in DMF-DMA. Further studies on the reaction mechanism, especially for methyl benzoates, are in progress.

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Scheme 2

Table 1. Synthesis of 1,3,5-triarylbenzene derivatives

entry ^a	β -nitro styrene (1)	products (% yield) ^{ref}
1	 1a	 2a (34%) ⁷
2	 1b	 2b (20%) ⁷
3	 1c	 2c (25%) ^{7,b}
4	 1d	 2d (40%) ⁹
5	 1e	 2e (37%) ⁹
6	 1f	no reaction
7	 1g	no reaction ^c
8	 1h	 3h (22%)
9	 1i	 3i (15%)

^aAll reactions were run on a 2 mmol scale. ^bTrace amounts of methyl *p*-chlorobenzoate was obtained. ^c*E* \rightarrow *Z* isomerization of **1g** (*E*) occurred to *E*:*Z* = 8 : 2.

search. The support of the Korea Basic Science Institute (Kwangju branch) is also acknowledged.

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- Characterization of **2d**: 75 mg (40%); mp 125-126 °C; ¹H NMR (CDCl₃) δ 6.51 (dd, *J* = 3.3 and 1.2 Hz, 3H), 6.77 (d, *J* = 3.3 Hz, 3H), 7.51 (d, *J* = 1.2 Hz, 3H), 7.87 (s, 3H); ¹³C NMR (CDCl₃) δ 105.72, 111.74, 118.05, 131.71, 142.31, 153.46; IR (KBr) 3148, 2925, 1608, 1498, 1014, 733 cm⁻¹; MS (70 eV) *m/z* (rel intensity) 138 (24), 152 (4), 165 (4), 189 (14), 219 (5), 247 (14), 276 (M⁺, 100).
- There was obtained enamino ketone derivative (Ph-COCH = CH-NMe₂) from the reaction of acetophenone and DMF-DMA in DMF. From the reaction of phenylacetylene and DMF-DMA, to our surprise, phenylpropargyl aldehyde was isolated in 52% yield.