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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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-nitrostyrene[3] and DMF-DMA in order to prepare 1,3,5-triarylbenzene derivatives, which are useful compounds in the fields of electrode and electroluminescent devices[4] 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, $TiCl_3(OTf)$ 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 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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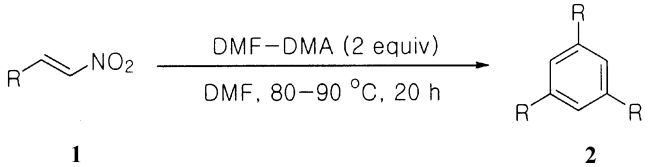
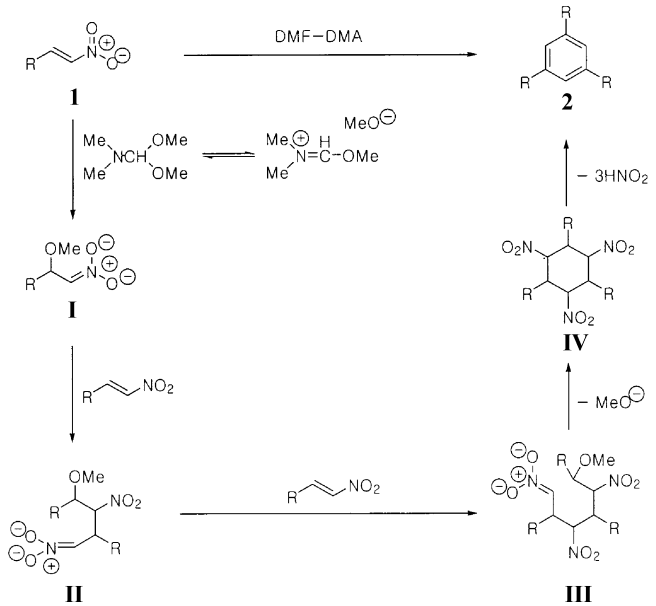


1 **2**

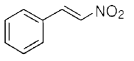
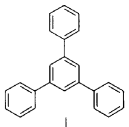
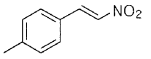
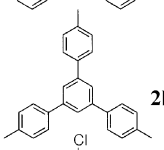
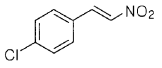
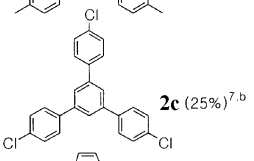
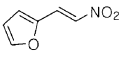
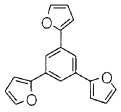
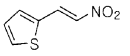
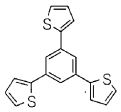
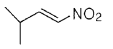
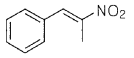
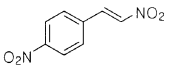
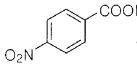
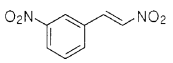
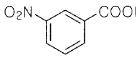
Scheme 1



I **II** **III** **IV**

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%)[8]
6	 **1f**	no reaction
7	 **1g**	no reaction[c]
8	 **1h**	 **3h** (22%)
9	 **1i**	 **3i** (15%)

[a]All reactions were run on a 2 mmol scale. [b]Trace amounts of methyl *p*-chlorobenzoate was obtained. [c]*E/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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5. (a) Viallat, A.; Pepin-Donat, B. *Macromolecules* **1997**, *30*, 4679. (b) Rebourt, E.; Pepin-Donat, B.; Dinh, E. *Polymer* **1995**, *36*, 399. (c) Pepin-Donat, B.; de Geyer, A.; Viallat, A. *Polymer* **1998**, *39*, 6673.
6. For transition metal catalyzed [2+2+2] cycloaddition reaction of phenyl acetylene derivatives, see (a) Meriwether, L. S.; Colthup, E. C.; Kennerly, G. W.; Reusch, R. N. *J. Org. Chem.* **1961**, *26*, 5155. (b) Jhingan, A. K.; Maier, W. F. *J. Org. Chem.* **1987**, *52*, 1161.
7. For acid catalyzed cyclic trimerization of acetophenones, see Iranpoor, N.; Zeynizaded, B. *Synlett* **1998**, 1079, and further references cited therein.
8. Tintiller, P.; Dupas, G.; Bourguignon, J.; Queguiner, G. *Tetrahedron Lett.* **1986**, *27*, 2357.
9. Characterization of **2d**: 75 mg (40%); mp 125-126 °C; ^{1}H NMR ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) 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).
10. There was obtained enamino ketone derivative (Ph-COCH = CH-NMe_2) 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.