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 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, TiCl₃(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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Scheme 1

Scheme 2
search. The support of the Korea Basic Science Institute (Kwangju branch) is also acknowledged.

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

<table>
<thead>
<tr>
<th>entry</th>
<th>$\beta$-nitro styrene (1)</th>
<th>products (% yield)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>![Diagram 1a]</td>
<td>2a (34%)</td>
</tr>
<tr>
<td>2</td>
<td>![Diagram 1b]</td>
<td>2b (20%)</td>
</tr>
<tr>
<td>3</td>
<td>![Diagram 1c]</td>
<td>2c (25%)</td>
</tr>
<tr>
<td>4</td>
<td>![Diagram 1d]</td>
<td>2d (40%)</td>
</tr>
<tr>
<td>5</td>
<td>![Diagram 1e]</td>
<td>2e (37%)</td>
</tr>
<tr>
<td>6</td>
<td>![Diagram 1f]</td>
<td>no reaction</td>
</tr>
<tr>
<td>7</td>
<td>![Diagram 1g]</td>
<td>no reaction</td>
</tr>
<tr>
<td>8</td>
<td>![Diagram 1h]</td>
<td>![Diagram 3h] (22%)</td>
</tr>
<tr>
<td>9</td>
<td>![Diagram 1i]</td>
<td>![Diagram 3i] (15%)</td>
</tr>
</tbody>
</table>

*All reactions were run on a 2 mmol scale.*
*Trace amounts of methyl $p$-chlorobenzoate was obtained.* $^{1}$E/Z isomerization of 1g (E) occurred to E/Z = 8 : 2.

7. For acid catalyzed cyclic trimerization of acetophenones, see Iranpoor, N.; Zeynizaded, B. *Synlett* 1998, 1079, and further references cited therein.
9. Characterization of 2d: 75 mg (40%); mp 125-126 °C; $^1$H NMR (CDCl$_3$): $^1$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, $J$ = 3.3 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.