Improved Synthesis of 1,3,5-Triarylbenzenes from α,β-Unsaturated Nitro Compounds

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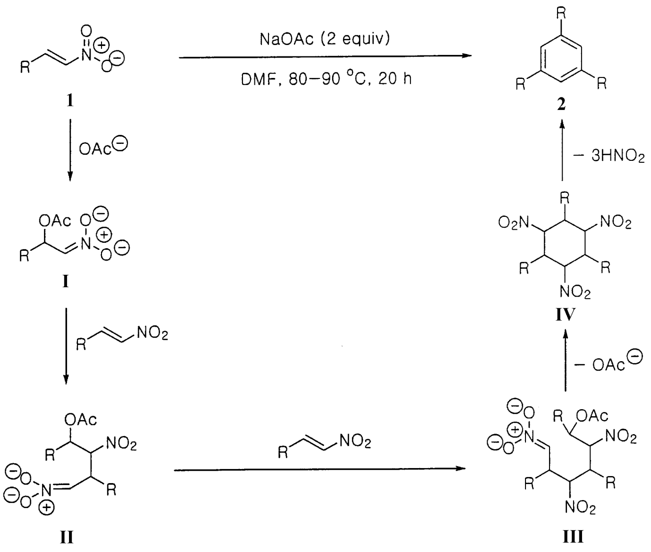
Received February 21, 2000

Recently we have reported that *N,N*-dimethylformamide dimethylacetal (DMF-DMA) could be used as a useful initiator for the cyclic trimerization of α,β-unsaturated nitro compounds to form 1,3,5-trisubstituted benzene derivatives.[1] In the reaction, trace amounts of methoxide ion in DMF-DMA might trigger the whole reaction.[1,2] However, the yields were not high enough to be practical in the synthetic point of view.[3]

Development of a new method for the preparation of 1,3,5-trisubstituted benzenes is important in view of their utility in the fields of electrode and electroluminescent devices[4] or in the chemistry of conducting polymers.[5] Most frequently used methods involve transition metal catalyzed cyclic trimerization of acetylene derivatives[6] and acid catalyzed trimerization of acetophenones.[7] In these contexts, we thought that the synthesis of 1,3,5-triarylbenzenes from α,β-unsaturated nitro compounds is a new entity for the preparation of these valuable compounds.

Thus, in order to find more efficient catalyst for the cyclic trimerization of α,β-unsaturated nitro compounds, we examined various candidates as a catalyst. These include sodium hydroxide, sodium methoxide, sodium acetate, potassium thioacetate, potassium cyanide, potassium iodide, potassium fluoride, and cesium fluoride *etc.* (see Table 1). We tried the reaction in DMF, DMSO, 1-methyl-2-pyrrolidinone (NMP), HMPA, methanol, and acetonitrile at rt -90 °C. Some represenatative trials were summarized in Table 1 by using β-nitrostyrene (**1a**) as a model substrate in various reaction conditions.



Scheme 1

Table 1. Cyclic trimerization of **1a** in various reaction conditions

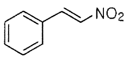
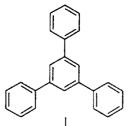
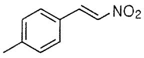
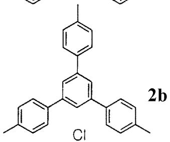
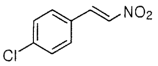
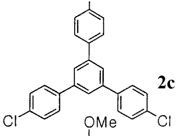
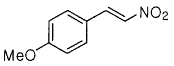
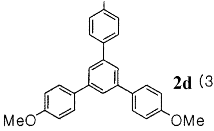
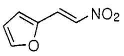
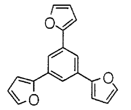
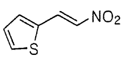
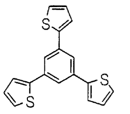
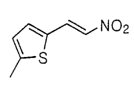
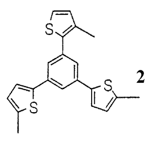
entry	solvent	initiator	reaction conditions	yield (%)
1	**DMF**	**DMF-DMA (2 equiv)**	**80-90 °C, 20 h**	**34** (ref. 1)
2	DMF	NaOH (1 equiv)	80-90 °C, 20 h	low yield
3	DMF	MeONa (2 equiv)	80-90 °C, 20 h	low yield
4	MeOH	MeONa (2 equiv)	reflux, 40 h	no reaction
5	DMF	$Me_2NCH(OEt)_2$ (2 equiv)	80-90 °C, 20 h	10
6	**DMF**	**NaOAc (2 equiv)**	**80-90 °C, 20 h**	**40**
7	DMF	KSAc (2 equiv)	80-90 °C, 20 h	low yield
8	DMF	KCN (2 equiv)	80-90 °C, 20 h	25
9	DMF	DABCO (2 equiv)	80-90 °C, 20 h	low yield
10	DMF	KI (4 equiv)	80-90 °C, 40 h	no reaction
11	DMF	Ph_3P (1 equiv)	80-90 °C, 20 h	low yield
12	DMF	KF (2 equiv)	80-90 °C, 20 h	low yield
13	DMF	CsF (2 equiv)	80-90 °C, 20 h	36
14	**DMSO**	**NaOAc (2 equiv)**	**80-90 °C, 24 h**	**41**
15	**NMP**	**NaOAc (2 equiv)**	**80-90 °C, 20 h**	**40**
16	**HMPA**	**NaOAc (2 equiv)**	**80-90 °C, 20 h**	**39**
17	CH_3CN	NaOAc (2 equiv)	reflux, 20 h	low yield
18	DMSO	KSAc (2 equiv)	80-90 °C, 20 h	low yield
19	DMF	NaOAc (2 equiv)	sonication, 60 °C, 20 h	29

As shown in Table 1, we could obtain 1,3,5-triphenylbenzene (**2a**) in increased yield when we use sodium acetate as a catalyst in polar, aprotic solvent such as DMF, DMSO, NMP, and HMPA (entries 6, 14-16). Some variations of the reaction conditions such as reaction temperature, amounts of NaOAc, or reaction time did not improve the yield of **2a** significantly. Thus considering yields, amounts of side products, and ease of separation, we decide to use NaOAc in DMF as the best conditions in our trials (entry 6 in Table 1, Scheme 1).

β-Nitrostyrene derivatives **1a-d** or heterocyclic analogues **1e-g** afforded the corresponding trimerized compounds **2a-g** in 34-66% isolated yields. The results were summarized in Table 2. However, alkyl derivatives (eg, 1-nitro-3-methyl-1-butene or 1-nitro-1-cyclohexene) or β-substituted nitro olefins (eg, 1-nitro-1-methyl-2-phenylethene) did not give the desired products. The failure might be due to the steric hindrance of the intermediates, **II** or **III**, generated by the consecutive Michael addition reaction (*vide infra*).

The mechanism for the formation of **2** can be proposed as shown in Scheme 1. Addition of acetate ion to β-nitrostyrene

Table 2. Synthesis of 1,3,5-triarylbenzene derivatives

entry[a]	*β*-nitro styrene (**1**)	products (**2**, % yield)[ref]
1	 **1a**	 **2a** (40%)[1,7a]
2	 **1b**	 **2b** (37%)[1,7a]
3	 **1c**	 **2c** (34%)[1,7a]
4	 **1d**	 **2d** (35%)[7b]
5	 **1e**	 **2e** (40%)[1]
6	 **1f**	 **2f** (66%)[1,7c]
7	 **1g**	 **2g** (60%)[7c]

[a]All reactions were run on a 2 mmol scale.

gave a new nucleophilic intermediate **I**, which adds to *β*-nitrostyrene to give **II**. Subsequent addition, same reaction once again, cyclization, and the final elimination of nitrous acid afford the desired product.[1,7f] Lewis basic nature of DMF must facilitate the elimination of nitrous acid in the last step.

In this report we developed an improved practical preparation method of 1,3,5-triarylbenzenes from the easily available *α*,*β*-unsaturated nitro compounds with the aid of sodium acetate in DMF.

Acknowledgments. We wish to thank the Chonnam National University Research Foundation for financial support of this work (1999).

References

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3. Reported yields of **2** in reference 1 by using DMF-DMA: **2a** (34%), **2b** (20%), **2c** (25%), **2e** (40%), **2f** (37%).
4. (a) Lindeman, S. V.; Struchkov, Yu. T.; Michailov, V. N.; Rusanov, A. L. *Izv. Akad. Nauk. Ser. Khim.* **1994**, 1986; *Chem. Abstr.* **1995**, *123*, 32717p. (b) Aslam, M.; Aguilar, D. A. *PCT Int. Appl. WO* 93 14,065; *Chem. Abstr.* **1993**, *119*, 270793x.
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