## Letters to the Editor

## Replacement of the nitro groups in 1,3,5-trinitrobenzene through the action of phenols; a general method for preparation of 3,5-dinitrophenyl aryl ethers and 5-nitroresorcinol diaryl ethers

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3,5-Dinitrophenyl aryl ethers (3,5-DNPAE) and 5-nitroresorcinol diaryl ethers inaccessible yet. At the same time, these compounds may be considered, for example, to be potential pesticides<sup>1,2</sup> and also as the starting compounds for preparing novel monomers for polycondensation.

We found a method for preparing 3,5-DNPAE based on nucleophilic substitution of a nitro group in 1,3,5trinitrobenzene (TNB) through the action of phenols containing both electron-donating and electron-withdrawing substituents in an amide type dipolar aprotic solvent\* (DMF, *N*-methylpyrrolidone, tetramethylurea, *etc.*). The reaction occurs in the presence of bases ( $K_2CO_3$  is the most efficient) at 80–90 °C over a period of 4–8 h. Using 2-naphthol and 3-pyridinol as examples we showed that not only phenols, but also other aromatic hydroxy compounds can be used.

Phenols incorporating two hydroxy groups (hydroquinone, 2,2-bis(4-hydroxyphenyl)propane) can be involved in this reaction (TNB :  $Ar(OH)_2$  2 : 1). The reaction yields the corresponding bis-3,5-dinitrophenyl ethers. When the reaction is carried out under more rigorous conditions (140-150 °C), the second nitro group can also be replaced to give the previously unknown 5-nitroresorcinol diaryl ethers. To prepare 5-nitroresorcinol diaryl ethers with identical aryl moieties (1) TNB was used, while derivatives with different aryl moieties (2) were prepared using 3,5-DNPAE.



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<sup>\*</sup> A non-amide-type solvent (DMSO) was inefficient (a low yield of 3,5-DNPAE).

Ethers (3) were prepared in a similar way.



3,5-DNPAE: Ar =  $RC_6H_4$  (R = H, 3-Me, 2-Me, 4-Br, 4-I, 4-F, 4-OH, 4-EtO, 4-COOH, 4-NH<sub>2</sub>, 3-NEt<sub>2</sub>, 4-MeCONH), 3-pyridyl, 2-naphthyl.

1:  $Ar = RC_6H_4$  (R = H, 2-Me, 3-Me, 4-EtO, 4-Br, 4-I, 4-COOH), 2-naphthyl, 3-pyridyl.

2: Ar, Ar' = Ph, 4-EtOC<sub>6</sub>H<sub>4</sub>; Ph, 4-IC<sub>6</sub>H<sub>4</sub>; Ph, 4-BrC<sub>6</sub>H<sub>4</sub>; Ph, 3-pyridyl; Ph, 4-FC<sub>6</sub>H<sub>4</sub>; Ph, 4-HOOCC<sub>6</sub>H<sub>4</sub>; 4-EtOC<sub>6</sub>H<sub>4</sub>, 3-MeC<sub>6</sub>H<sub>4</sub>.

**3**: Y is the corresponding moiety of hydroquinone, 2,2-bis-(4-hydroxyphenyl)propane, 2,2-bis(4-hydroxyphenyl)hexafluoropropane, or 4,4'-dihydroxydiphenyl sulfone. Through the action of phenols, even the nitro group in 5-nitroresorcinol diaryl ethers can be replaced, *i.e.*, activation by other nitro groups is not required. This was shown using the reaction of 1 (R = Ph) with phenol (in *N*-methylpyrrolidone in the presence of  $K_2CO_3$ , 200 °C, 2 h) as an example. This reaction affords the known<sup>3</sup> triphenyl phloroglucinol ether.

3,5-DNPAE and compounds 1-3 prepared for the first time were characterized by <sup>1</sup>H, <sup>13</sup>C, and <sup>14(15)</sup>N NMR, IR, and mass spectra and also by the elemental analysis data.

## References

- N. N. Mel'nikov, Pestitsidy. Khimiya, tekhnologiya, primenenie [Pecticides. Chemistry, Technology, and Use], Khimiya, Moscow, 1987, 123 (in Russian).
- T. Yoshimoto, K. Igarashi, T. Fujita, and T. Harayama, J. Pesticide Sci., 1990, 15, 341.
- 3. F. Ullman and P. Sponagel, Chem. Ber., 1905, 38, 2211.

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## Palladium catalyzed cross-coupling of symmetrical diaryliodonium salts with sodium tetraphenylborate in water

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It has been shown previously that palladium-catalyzed reactions of aryl halides with organoboron compounds,<sup>1</sup> olefins,<sup>2,3</sup> carbon oxide,<sup>4</sup> and terminal acetylenes<sup>5</sup> occur in water at high rates and with high yields. Apart from aryl halides, diaryliodonium salts can be used in the catalytic reactions.<sup>6–8</sup>

We found that in the presence of catalytic amounts of PdCl<sub>2</sub>, symmetrical diaryliodonium salts readily react with sodium tetraphenylborate when heated in water, irrespective of the nature of X, to give the corresponding diaryls in high yields. For participation of all four of the phenyl groups in Ph<sub>4</sub>BNa in the reaction, the presence of a base, Na<sub>2</sub>CO<sub>3</sub>, is necessary:

2 Ar<sub>2</sub>IX + Ph<sub>4</sub>BNa 
$$\frac{1 \text{ mol.\% PdCl}_2}{\text{Na}_2\text{CO}_3, \text{ H}_2\text{O}}$$
 4 Ar—Ph  
96—98 %  
X = HSO<sub>4</sub>, BF<sub>4</sub>, CF<sub>3</sub>COO

 $Ar = m - NO_2C_6H_4, p - FC_6H_4, Ph$ 

The reaction occurs in two steps:

1. 
$$Ar_2IX + \left[Ph - B \leftarrow \right] \xrightarrow{"Pd"} Ar - Ph + ArI + \left[X - B \leftarrow \right]$$
  
2.  $ArI + \left[Ph - B \leftarrow \right] \xrightarrow{"Pd"} Ar - Ph + \left[I - B \leftarrow \right]$ 

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