

Note

Rapid synthesis of nitro substituted diaryl ethers under mild conditions

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Various nitro substituted diaryl ethers have been synthesized rapidly by using polymer supported phenoxide anions and halides under mild conditions. The isolation of pure products by simple filtration and evaporation is an important feature of this method.

There is an immense need in industry for an explosive composition which would be safe, reliable and stable at elevated temperature. For example, it is sometimes necessary to shoot explosive devices in hot wells at temperatures which may reach as high as 200-300 °C. In the steel industry, open hearth furnaces are tapped with explosive shaped charges in tap holes at temperatures above 500 °C. Using the explosives available at present which have the best possible thermal properties, it is necessary to jacket the shaped charges with heavy insulation. Even so, the charge must be initiated within 3-4 min from the time it is set in place or it may fail due to thermal instability.

There is also a growing demand in connection with space programmes for explosive compounds which are stable at elevated temperatures and low pressure¹. The explosive stores carried externally on high speed aircraft at low altitude are subjected to aerodynamic heating which may raise the temperature of the filling above 80 °C, so that the Torposes [RDX/TNT] and other conventional explosives are unsuitable for such stores².

Explosives with improved temperature properties, usually called as "Heat Resistant Explosives" have emerged to meet such requirements. Nitro compounds have been found to be very useful heat resistant explosives^{3,5}. They are of special interest because of

their ability to withstand the high temperature and low pressure encountered in space applications^{1,4}. No doubt, that the temperature of these explosives is highly crucial. Sometimes, even complex synthetic routes can be adopted, provided the product exhibits the requisite properties, a low vapour pressure and the ability to function satisfactorily after appropriate environmental trials, which may include heating at temperatures as high as 250 °C.

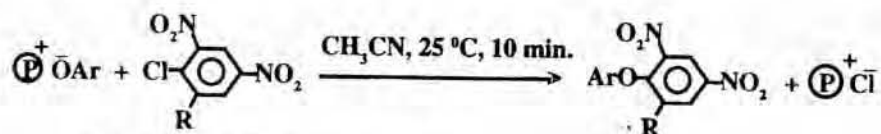
Considering the importance of nitro compounds as heat resistant explosives, we are interested in the synthesis of nitro substituted diaryl ethers under mild conditions. Polymer supported phenoxide anions were treated with different halides at 25 °C to give corresponding diaryl ethers within a very short time (10 min.) (Scheme I).

The results are summarised in the Table I. This method combines the advantage of solid phase synthesis and anionic activation, avoids tedious reaction work-up procedure. The resin could be used repeatedly, since its initial activity could be regenerated. These nitro substituted diaryl ethers are found to be useful insensitive explosives^{2,5}.

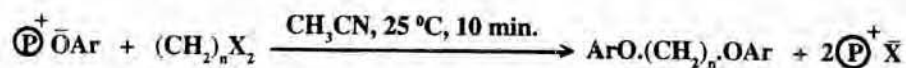
Experimental Section

All reactions were conducted in oven dried flasks. Solvents were distilled before use. All phenols were purified by crystallisation/distillation. Picryl chloride was prepared⁶ in the laboratory using picric acid, pyridine and POCl₃. Strong anion exchange resin, Tulsion A-27 (Cl⁻ form), was procured from Thermax Chemicals, Bhosari, Pune. Products were characterised by IR and ¹H NMR.

General method for the preparation of polymer-supported phenoxide anion. Substituted phenol (25 mmoles) was dissolved in NaOH (50 mL, 25 mmoles). Tulsion A-27 (Cl⁻ form, 5g) was added to the above solution and stirred for 1 hr. Then the resin was filtered, washed with distilled water till it was free from chloride ions and excess of phenoxide ion (15 mmoles). The resin was washed with ethanol, ether and then dried at 50 °C *in vacuo* for 2 hr. The capacity of phenoxide supported resin was found to be 2 mmoles/g of dry resin.



R=H, NO₂, Ar = Substituted aryl



n = 2, 4; Ar = 2, 4, 6- trinitrophenyl; X= Br

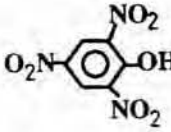
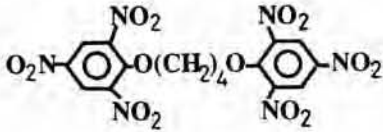
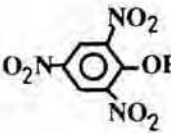
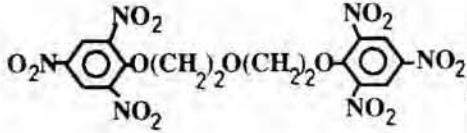
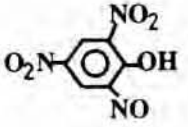
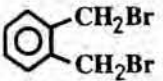
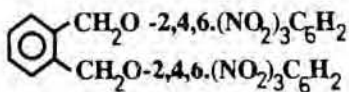
Scheme 1

Table I : Synthesis of nitro substituted diaryl ethers at 25°C

Entry	Phenol	Halide	Product	m.p. (°C) Obs. (Lit)	Yield (%)
1				125 [126] ^B	80
2				94 [94] ^B	82
3				120 [120] ^B	86
4				127 [128] ^B	90
5				95 [95] ^B	93
6				97 [95] ³	71
7				118 [118] ⁴	80
8		Br.(CH ₂) ₂ .Br		129 [128] ⁴	70

Contd.

Table I — Synthesis of nitro substituted diaryl ethers at 25 °C —Contd.

Entry	Phenol	Halide	Product	m.p. (°C) Obs. (Lit)	Yield (%)
9		Br.(CH ₂) ₄ .Br		116 [117] ⁴	62
10		Br.(CH ₂) ₂ O.(CH ₂) ₂ Br		123 [125] ³⁻⁶	70
11				109 [110] ³⁻⁶	81

General method for the synthesis of nitro substituted diaryl ethers. A mixture of phenoxide anion supported on Tulsion A-27 (5g, 10 mmoles) in acetonitrile (20 mL) and monohalide (5 mmoles) or dihalide (2.5 mmoles) was stirred for 10 minutes. The reaction was monitored by TLC. After completion of the reaction, the mixture was filtered, washed with ether (3 × 10 mL). Removal of the solvent under reduced pressure gave the corresponding ether product in good yield (based on halide) and in almost pure form (characterised by m.p., I.R., ¹H NMR and comparison with authentic samples)

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References

- This paper has been dedicated to Prof. M S Wadga (University of Pune) on the occasion of his 60th birthday and it is in the series of solid supported reagents and reactions part 22. For Part 21, see B P Bandgar & S B Pawar, *J Chem Res (S)* 1998, 212.
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