

## Synthesis of Nitroalkanes from Alkylhalides under Mild and Nonaqueous Conditions by Using Polymer Supported Nitrites

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Alkyl halides are efficiently converted to their corresponding nitroalkanes under mild and nonaqueous conditions by using polymer supported nitrites. The polymeric reagent is regenerable.

**Keywords:** Polymer supported nitrites; Nitration; Nonaqueous condition; Polymeric reagent.

### INTRODUCTION

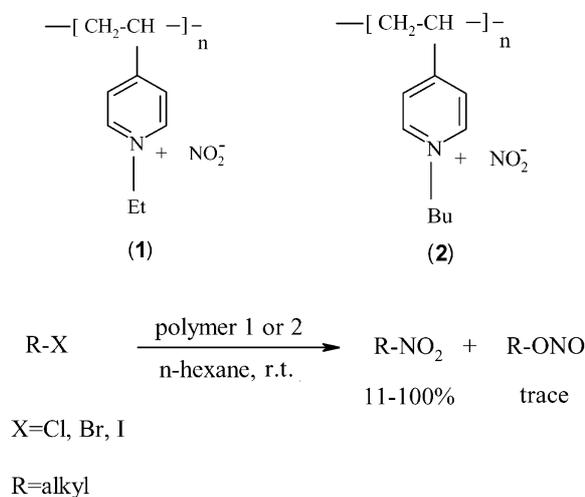
Polymer supported reagents, especially anion exchange resins, have been widely applied in organic synthesis.<sup>1-7</sup> These polymeric reagents are generally used in single step reactions. Their main advantage over monomeric reagents is their insolubility in the reaction medium and consequently the easier workup by a simple filtration. The reactions can often be driven to completion by using an excess of these reagents without the fear of separating the unspent reagent from the desired products. The spent polymeric reagents can usually be removed quantitatively and regenerated. In addition, anions bound to the macroporous resin have the advantage that they often react successfully in non-polar solvents.

There are many reports in the literature for preparation of nitroalkanes and the most general one has been the conversion of alkyl halides to nitroalkane with metal nitrites such as AgNO<sub>2</sub> or NaNO<sub>2</sub><sup>8</sup> and amberlite -900 supported nitrite.<sup>9</sup> Sodium nitrite, however, has been the reagent most widely used. In general each of these reagents suffer from at least one of the following drawbacks: 1) aqueous medium has to be used; 2) low yield; 3) reaction to be carried out in the presence of phase transfer catalysts; 4) difficult workup; and 5) formation of the alkylnitrite byproducts in high yield (15-60%).

Now we wish to report an improved, efficient and easy method for synthesis of nitroalkanes from alkyl halides by using a polymer supported nitrite under mild and nonaqueous condition in high yields (Scheme I). Crosslinked poly(N-ethyl-4-vinylpyridinium)nitrite [P<sub>4</sub>-Et] NO<sub>2</sub> (**1**) and crosslinked poly(N-butyl-4-vinylpyridinium)nitrite [P<sub>4</sub>-Bu] NO<sub>2</sub> (**2**) were prepared by an exchange reaction between cross-

linked poly(N-ethyl-4-vinylpyridinium)iodide [P<sub>4</sub>-Et] I or crosslinked poly(N-butyl-4-vinylpyridinium)bromide [P<sub>4</sub>-Bu] Br with a slight excess of sodium nitrite in water. Using these heterogeneous reagents converted alkyl halides to nitroalkanes in n-hexane and proved to be the solvent of choice among other non-polar organic solvents (Table 1). In these conversions the best molar ratio of reagent/substrate proved to be equal to 2.

**Scheme I**



The advantages of this method are: 1) the reaction can be performed in non-aqueous medium; 2) an excess of the reagent can be used; 3) the product can be obtained by simple filtration and evaporation of the solvent; 4) the polymeric reagent is easily regenerable; and 5) waste and byproducts can be minimized.

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Table 1. Conversion of alkylhalides to corresponding nitroalkanes using [P<sub>4</sub>-Et] NO<sub>2</sub> (1) or [P<sub>4</sub>-Bu] NO<sub>2</sub> (2) in n-hexane at room temperature

Entry	Substrate	Product <sup>a</sup>	b.p or (m.p) °C	[P <sub>4</sub> -Et] NO <sub>2</sub> (1) time(h)/yield <sup>b</sup> (%)	[P <sub>4</sub> -Bu] NO <sub>2</sub> (2) time(h)/yield <sup>b</sup> (%)
1	Iodoethane	Nitroethane	110-114	38/100 <sup>c</sup>	33/100 <sup>c</sup>
2	1-Iodopropane	1-nitropropane	128-130	43/100 <sup>c</sup>	-
3	1-Iodobutane	1-nitrobutane	147-152	48/100 <sup>c</sup>	42/100 <sup>c</sup>
4	1-Iodooctane	1-nitrooctane	-	72/58	72/66
5	1-Iodododecane	1-nitrododecane	-	72/17	72/21
6	2-Iodobutane	2-nitrobutane	135-140	72/65	72/72
7	Iodocyclohexane	nitrocyclohexane	(33-35)	72/56	72/62
8	1-bromobutane	1-nitrobutane	147-152	72/82	72/90
9	1-bromooctane	1-nitrooctane	-	72/51	72/51
10	2-bromopropane	2-nitropropane	118-122	72/63	72/59
11	2-bromobutane	2-nitrobutane	135-140	72/54	-
12	bromocyclohexane	nitrocyclohexane	(33-35)	72/41	72/47
13	4-bromobenzyl bromide	4-bromophenyl nitromethane	-	17/100 <sup>c</sup>	13/100 <sup>c</sup>
14	benzylchloride	phenylnitro- methane	-	72/88	72/93
15	chlorodiphenyl- methane	nitrodiphenyl- methane	-	72/11	72/16
16	chlorocyclo- hexane	nitrocyclohexane	(33-35)	72/26	72/31
17	2-chloro-2- methylpropane	-	-	72/0	72/0

<sup>a</sup> The structures were confirmed by comparison of the boiling point, melting point, IR and NMR spectra with those of authentic specimen.

<sup>b</sup> isolated yields.

<sup>c</sup> conversion percent.

## RESULTS AND DISCUSSION

Crosslinked polymers (1) and (2) can be easily prepared and used as mild and efficient polymeric reagents for conversion of alkylhalides to the corresponding nitroalkanes. One of the advantages of this method is formation of a little alkyl nitrite as a byproduct, because the nitrite ion tightly bonded to the pyridinium pendant group of polymer and nitrite ion can react with alkyl halide at a nitrogen site to give the nitroalkane. In comparison results obtained from polymer (1) and (2) (Table 1), we concluded that yields of nitroalkanes from Polymer (2) were higher than polymer (1), because the larger alkyl group on nitrogen in polymer (2) decreases the interaction between the nitrite ion and the pyridinium pendant group of polymers, and it can react with alkyl halide faster than polymer (1).

Moreover, the order of reactivity of alkylhalides was R-I > R-Br > R-Cl. The larger R group in alkylhalide decreased its activity. The activity of alkylhalides was: 1° > 2° > 3°.

## EXPERIMENTAL

### General

Crosslinked poly(4-vinylpyridine) (2% divinylbenzene) was purchased from the Fluka Company. All nitroalkane products were identified by comparison of their M.P, B.P, IR and <sup>1</sup>H NMR spectra and physical data with those of authentic samples. Reaction monitoring and the purity of the products were accomplished by GLC and TLC. IR and <sup>1</sup>H NMR spectra were recorded on a Perkin-Elmer IR-157-G and a Hitachi R-2413 60 MHz spectrophotometer, respectively.

### Preparation of crosslinked poly(N-ethyl-4-vinylpyridinium)nitrite. [P<sub>4</sub>-Et] NO<sub>2</sub>

Crosslinked poly(4-vinylpyridine) (20 mmol, 2.12 g) was treated with ethyl iodide (20 mmol, 3.24 g) in acetonitrile (10 mL) and stirred for 24 hr at room temperature. The quaternized polymer [P<sub>4</sub>-Et] I was filtered and washed with distilled water and acetonitrile. It was then dried under vacuum in the presence of P<sub>2</sub>O<sub>5</sub> at 40 °C.

To 40 mL of a 3 M solution of sodium nitrite was added [P<sub>4</sub>-Et] I and slowly stirred for 24 hr. The resin [P<sub>4</sub>-Et] NO<sub>2</sub> was filtered off and washed rapidly with distilled water until the filtrate gave a negative test for NO<sub>2</sub><sup>-</sup>. It was then washed with ether and dried under vacuum in the presence of P<sub>2</sub>O<sub>5</sub> at 40 °C (1.6 g).

The activity of these polymers was determined by potentiometric titration with a 0.1N solution of silver nitrate. The activity of polymer (1) was 4.8 mmol/g of the polymer, and the activity of polymer (2) was 3.7 mmol/g of the polymer.

#### General procedure for conversion of alkylhalides to corresponding nitroalkanes

To a mixture of alkylhalide (1 mmol) and n-hexane (10 mL) in a round-bottomed flask (50 mL), 2 mmol of polymer (1) or (2) was added, and the mixture stirred at room temperature for 17-72 hr (Table 1). The formation of nitro compounds was monitored by TLC (eluent: chloroform) or GLC. On completion of reaction, the mixture was filtered and washed with n-hexane and ether. The combined filtrate was evaporated to obtain nitroalkanes in 11-99% yield. The spent polymeric reagent was regenerated by treatment with sodium nitrite solution. The regenerated reagent has the same capacity as the original form.

#### Preparation of nitroethane from iodoethane by using polymer (2): A typical procedure

To a mixture of iodoethane (0.4 mL, 5 mmol) and n-hexane (10 mL) in a round-bottomed flask (50 mL), 10 mmol of polymer (2) (2.7 gr) was added, and the mixture stirred at room temperature for 33 hr. The formation of product was monitored by GLC. On completion of reaction, the mixture

was filtered and washed with n-hexane and ether. The combined filtrate was evaporated to obtain nitroethane. b.p = 110-114 °C, <sup>1</sup>H NMR, δ (ppm): 4.3 (q, 2H), 1.38 (t, 3H).

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#### REFERENCES

1. Sherrington, D. C.; Hodge, P. In *Synthesis and Separations Using Functional Polymers*; John Wiley & Sons, 1988.
2. Sherrington, D. C.; Hodge, P. In *Polymer Supported Reactions in Organic Synthesis*; John Wiley & Sons, 1980.
3. Takemoto, K.; Inaki, Y.; Ottenbrite, R. M. In *Functional Monomers and Polymers*; Marcel Dekker Inc.: New York, 1987.
4. (a) Akelah, A.; Sherrington, D. C. *Chem. Rev.* **1981**, *81*, 577. (b) Akelah, A.; Sherrington, D. C. *Polym.* **1984**, *24*, 1369.
5. Steven, V. L.; Ion, R. B.; Robert, N. B.; Philip, S. J.; Andrew, G. L.; Deborah, A. L.; Marcella, N.; James, S. S.; Storer, R. I.; Stephen, J. T. *J. Chem. Soc. Perkin Trans. 1* **2000**, 3815.
6. Tamami, B.; Iranpoor, N.; Karimi Zarchi, M. A. *Polymer* **1993**, *34*, 2011.
7. Tamami, B.; Karimi Zarchi, M. A. *Eur. Polym. J.* **1995**, *31*, 715.
8. *Principles of Organic Synthesis*; Chapman & Hall: Norman, R. O. C., 1978; pp 557-559.
9. Gelbard, G.; Colonna, S. *Synthesis* **1977**, 113.