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Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: <u>http://www.tandfonline.com/loi/lsyc20</u>

Polymer Supported Reagents: Oxidative Selection Between Thiols

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To cite this article: F. Shirini , M. M. Lakouraj , I. Mohammadpour-Baltork & D. Asadi (2003) Polymer Supported Reagents: Oxidative Selection Between Thiols, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 33:11, 1833-1837, DOI: <u>10.1081/SCC-120020192</u>

To link to this article: <u>http://dx.doi.org/10.1081/SCC-120020192</u>

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SYNTHETIC COMMUNICATIONS[®] Vol. 33, No. 11, pp. 1833–1837, 2003

Polymer Supported Reagents: Oxidative Selection Between Thiols

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ABSTRACT

A very simple reaction is described for the efficient oxidative selection between thiols by Dowex 1-X8, as a quaternary ammonium resin, on which Cl^- is replaced by dichromate and bisulfate ions (DDB).

Key Words: Dowex 1-X8; Oxidation; Polymer supported reagents; Selection; Thiols.

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Oxidative coupling of thiols to disulfides under heterogeneous, neutral, and mild conditions is of importance from biological and practical points of view.^[1,2] Since thiols are easily oxidizable and may thus be overoxidized, extensive studies have been carried out to discover methods for their controlled oxidation.^[3–15] However, some of the reported reagents suffer from disadvantages such as long reaction time, difficulty of preparation, difficult work-up, low selectivity, and instability. Thus, a milder and more selective reagent is still in demand.

In this communication we report that Dowex 1-X8, on which Cl^- is replaced by $Cr_2O_7^{2-}$; and HSO_4^- (DDB), as a previously reported oxidizing agent,^[16] can act as a very efficient reagent for the coupling of thiols in refluxing acetonitrile, in good to high yields (Table 1). Overoxidation of the products was not observed by this method.

Entry	Substrate	Time (min)	Yield (%) ^a
1	— SH	15	90
2	сі — 💭 зн	10	92
3	Me	5	85
4	SH	25	90
5	HO SH	40	85
6	HS AN SH	20	b
7	N SH	30	75
8	SH	90	80
9	CH ₂ SH	90	0^{c}
10	Me — CH ₂ SH	90	0^{c}

Table 1. Oxidative coupling of thiols with DDB in refluxing acetonitrile.

^aIsolated yield.

^bPolymerization was occurred.

^cReaction was not occurred and the unchanged starting material was obtained.

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Scheme 1.

Table 2. Comparison of some of the results obtained by our method (1) with some of those obtained by *bis*[trinitratocerium(IV)] chromate (2),^[6] pyridinium chlorochromate (3),^[6] and pyrazinium dichromate (4).^[15]

Entry	Substrate	Time in hour (yield %)			
		1	2	3	4
1	Thiophenol	0.25 (90)	4 (90)	2 (85)	0.7 (91)
2	2-Mercaptobenzothiazole	1.5 (80)	4 (80)	4 (50)	3.5 (94)

Benzylic thiols do not undergo oxidation with this reagent (Table 1, Entries 9 and 10). Therefore this methodology shows selectivity and is suitable for oxidative selection against thiols. This is exemplified by the competitive reaction between thiophenol and benzylthiol (Sch. 1).

In order to show the efficiency of this method we have compared some of the results with relevant ones reported in the literature (Table 2).^[6,15]

In conclusion, this method is very simple and efficient for oxidative selection between thiols. The easy procedure and simple work-up, simplicity, selectivity, and short reaction time make this method a useful addition to the present methodologies.

EXPERIMENTAL

All products were characterized through comparison of their spectral and physical data with those of the known samples.^[17] The purity determination of the products was accomplished by TLC on silica gel polygram SIL G/UV 254 plates. Dowex 1-X8 (Cl⁻ form, 20–50 mesh) and other chemicals were purchased from Merck. Products were separated

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and purified by different chromatography techniques, and were also identified by the comparison of their m.p., IR and NMR spectra, b.p., refractive index with those reported for the authentic samples. The capacity of the reagent was determined by atomic absorption technique and titration method.

Preparation of DDB

To a solution of CrO_3 (0.35 g, 3.5 mmol) in 0.5 M H₂SO₄ (40 mL),^[18] Dowex 1-X8 (5 g) was added and the mixture stirred for 0.5 h at room temperature. The resulting dark-orange resin was filtered and washed with acetone (2 × 20 mL) and diethylether (2 × 5 mL) and was finally dired in vacuo at 50°C for 0.5 h. The infrared spectrum of the dry reagent showed bands at 930 and 765 cm⁻¹, characteristic of dichromate ion and bands at 820, 847, 877, 1045, 1180, 1220, 1420, and 3250 cm⁻¹, characteristic of bisulfate ion.^[19]

The capacity of the reagent was determined to be $0.25 \text{ mmol } \text{Cr}_2 \text{O}_7^{2-}$ and $1.5 \text{ mmol } \text{HSO}_4^{-}$ per gram of the resin.

General Procedure for the Oxidation of Thiols by DDB

To a solution of thiol (1 mmol) in acetonitrile (5 mL), DDB (2 mmol, based on capacities) was added and refluxed while stirred for 5-90 min. Progress of the reaction was monitored by TLC. The reaction mixture was cooled to the room temperature and filtered being followed by repeated washing with acetonitrile (10 mL). Evaporation of the solvent followed by column chromatography on silica gel gave the corresponding disulfide from good to high yields.

Regeneration of Dowex 1-X8 in its Cl^- form: To an aqueous solution of NaOH (2 M, 20 mL) the spent reagent (2 g) was added and the mixture was stirred for 12 h. The suspension was filtered and washed repeatedly with a solution of hydrochloric acid (2 M) and finally with water. The precipitate was dried in vacuo at 80°C for 6 h to give the original quaternary ammonium resin characterized by its IR spectrum.

ACKNOWLEDGMENT

We are grathful to Guilan University Research Council for financial support of this work.

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Received in the Netherlands August 23, 2002



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