

Gholamabbas Chehardoli,^{a,*} Mohammad Ali Zolfigol,^b Ezat Ghaemi,^b Elaheh Madrakian,^b Khodabakhsh Niknam,^c and Shadpour Mallakpour^{d,e}

^aSchool of Pharmacy, Hamedan University of Medical Sciences, 65178 Hamedan, Iran

^bFaculty of Chemistry, Bu-Ali Sina University, Hamedan, Iran

^cDepartment of Chemistry, Faculty of Sciences, Persian Gulf University, Bushehr, Iran

^dDepartment of Chemistry, Organic Polymer Chemistry Research Laboratory, Isfahan University of Technology, Isfahan 84156-83111 Iran

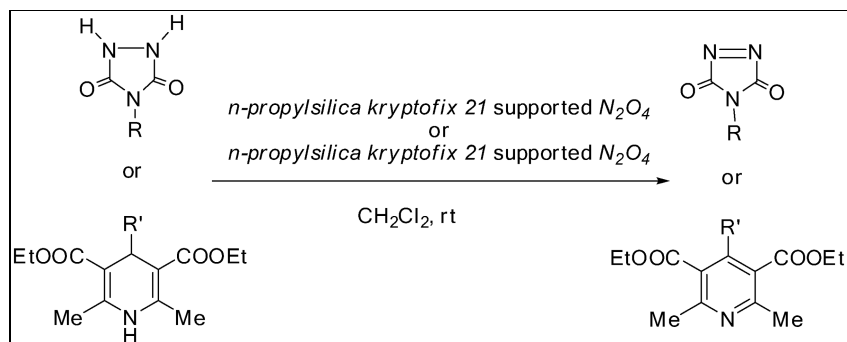
^eNanotechnology and Advanced Materials Institute, Isfahan University of Technology, Isfahan 84156-83111, Iran

*E-mail: chehardoli@umsha.ac.ir or cheh1002@gmail.com

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3-Chloropropylsilica was reacted with Kryptofix 21 or 22 in the presence of triethylamine to form *N*-propylsilica Kryptofix 21 and Kryptofix 22. Then N_2O_4 was added to each of these polymers to chemisorb onto cavity of aza-crown ethers. These functionalized polymers were applied for the fast and simple oxidation of urazoles and 1,4-dihydropyridines, respectively.

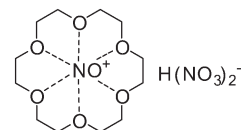
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INTRODUCTION

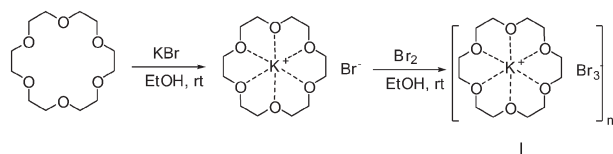
Crown ethers have attracted significant attention from various fields of science and technology. Crown ether moieties are popular host compounds in host-guest chemistry and these ligands have shown a remarkable ability to form strong complexes with organic and inorganic cations [1,2] or anions [3] selectively. Recently, we reported $\{[K.18\text{-crown-6}]Br_3\}_n$ as a unique tribromide type and columnar nanotube-like structure (**I**; Scheme 1) [4].

Polymer-supported reagents and catalysts have been widely applied in organic transformations. Immobilization of reactive species on a polymer support could provide many important advantages over analogous homogeneous systems; for example separation of the support from the reaction mixture can be achieved by simple filtration aiding isolation and purification procedures, excess of a polymeric reagent can be readily employed without incurring a penalty in work-up, transition metal complexes and optically active catalysts might be efficiently retained for reuse, and noxious or toxic species might be encapsulated when bound to a macromolecule, with obvious advantages in environmental terms [5–7].

For over a century, dinitrogen tetroxide has found wide application in organic synthesis and transformations, such as nitration of aromatic compounds, nitroization of amines, preparation of thionitrite and sulfinyl nitrites, oxidation of olefins, and dethioacetalization reactions [8]. Apart from difficulties in handling the poisonous and corrosive dinitrogen tetroxide, the biggest disadvantage of using gaseous N_2O_4 in organic reactions is its high reactivity, which usually causes undesired side reactions. To overcome the above mentioned limitations some reports are published on the use of N_2O_4 complexes of organic [9], polymeric [10], and inorganic compounds [11] as useful reagents in organic reactions. In 2001, we reported $[NO^+ \cdot Crown \cdot H(NO_3)_2^-]$ (**II**) as a crown ether-supported N_2O_4 for some organic transformations [12].



II

Scheme 1. Preparation of {[K.18-crown-6]Br₃]_n.

Given the usefulness of such compounds, the development of further synthetic protocols for the synthesis of new supported N₂O₄ compounds is an area of interest. In this article, we report preparation of *n*-propylsilica kryptofix 21 and kryptofix 22-supported N₂O₄ and application of them in the oxidation of urazoles and 1,4-dihydropyridines, respectively.

RESULTS AND DISCUSSION

In continuation of our studies on the host-guest chemistry of crown ethers [4,12], the synthesis and application of supported N₂O₄ compounds [10d,11], the oxidation of urazoles and 1,4-dihydropyridines [14], and application of PVP-H₂O₂ for the epoxidation of α,β -unsaturated ketones [15], we found that 3-chloropropylsilica (**1**) [13] was reacted with kryptofix 21 or 22 in the presence of triethylamine to form *n*-propylsilica kryptofix 21 (**III**) and kryptofix 22 (**IV**), respectively. The resulting composites were characterized by FT-IR and XRD. Then N₂O₄ was added to each of these polymers to chemisorb onto cavity of aza-crown ethers and two new crown ether-based polymeric-supported N₂O₄ (**V** or **VI**) were synthesized (Scheme 2).

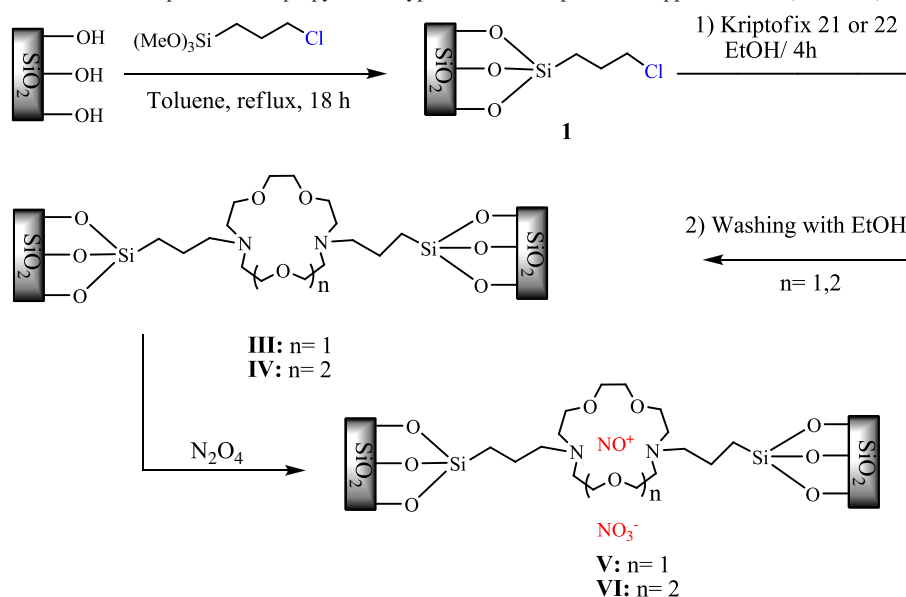
In the next step, we decided to apply these functionalized polymers for the oxidation of urazoles and 1,4-dihydropyridines, respectively. A wide range of urazoles and 1,4-dihydropyridines was subjected to the rapid oxidation in the presence of *n*-propylsilica kryptofix 21 or kryptofix 22-supported N₂O₄ (**V** or **VI**) in dichloromethane at room temperature under mild, heterogeneous, and metal-free conditions. All products are obtained with good to excellent yields (Scheme 3 and Table 1).

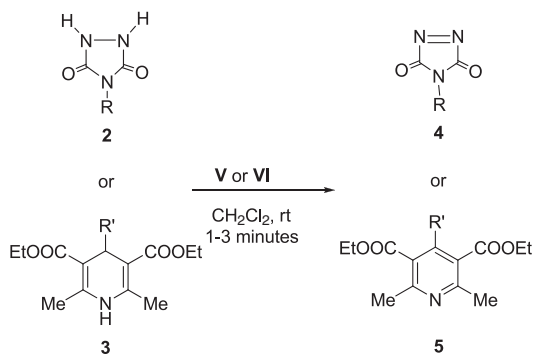
Oxidation of urazoles and 1,4-dihydropyridines to their corresponding triazolinediones and pyridines with *n*-propylsilica kryptofix 21 or kryptofix 22-supported N₂O₄ (**V** or **VI**) offers the following advantages: (a) in comparison with very toxic N₂O₄, **V** or **VI** are very safe and easy-handling, (b) the procedure is highly efficient, (c) the yields of products are high, (d) reaction procedure and work-up of products is very simple, because **V** or **VI** are insoluble in CH₂Cl₂ and are excellent NO⁺ mediated sources for the organic reactions under heterogeneous conditions, (e) despite some previously reported procedures [14], this oxidation reaction did not need water, (f) reaction time is very low, and (g) procedure is metal-free and matches with green chemistry protocols.

EXPERIMENTAL

Preparation of *n*-propylsilica kryptofix 21 and kryptofix 22-supported N₂O₄.

To a magnetically stirred mixture of 3-chloropropylsilica [13] (10 g) in dry CHCl₃ (20 mL), kryptofix 21 or kryptofix 22 (2.5 mmol) and some drops of triethylamine were added and refluxed for 24 h. Then, the mixture was filtered and washed with dichloromethane (3 × 10 mL) and ethanol (3 × 10 mL). After drying in oven, silica bonded

Scheme 2. Preparation of *n*-propylsilica kryptofix 21 and kryptofix 22-supported N₂O₄ (**V** and **VI**).

Scheme 3. Urazols and dihydropyridines used in the oxidation reaction.

2	R	3	R'
a	Me	a	H
b	Et	b	Me
c	<i>n</i> -Propyl	c	Ph
d	<i>n</i> -Butyl	d	3-Nitrophenyl
e	4-Cyclohexyl	e	4-Nitrophenyl
f	Ph	f	2-Furyl
g	(4- <i>t</i> -Bu)-ph	g	2-Methoxy phenyl
h	(4-Ph-CH ₂ -Ph-4')-bis		
i	4-Nitrophenyl		
j	3,4-Dichlorophenyl		
k	4-Chlorophenyl		
l	4-Methoxy phenyl		

n-propylsilica cryptand 21 was obtained as white powder [III, 10.32 g] and *n*-propylsilica cryptand 22 [IV, 10.34 g].

To a 250-mL one-necked round-bottomed flask was charged 45.0 g of dried fine powder lead (II) nitrate. The flask was equipped with a 35-cm column and was connected to a trap through a polyethylene tube. The trap was connected to the gas inlet tube. The lead (II) nitrate was heated with a bunsen burner. Brownish red NO₂-N₂O₄ gas evolved, and it was bubbled slowly through the cold *n*-propylsilica kryptofix 21 and kryptofix 22 (10.0 g) in CH₂Cl₂ mixture (25 mL) for 30 min. After a few minutes, a deep-red color appeared. The temperature was kept below 0°C. The red mixture was allowed to stir for another 60 min, and then dry N₂ gas was bubbled through the solution to extrude the excess of NO₂ gas and then the solvent was evaporated. The obtained solid was dried under vacuum to give *n*-propylsilica kryptofix 21 and kryptofix 22-supported N₂O₄ as yellow powder. These reagents could be stored in the refrigerator for several months without losing activity.

General procedure for the oxidation of urazoles and 1,4-dihydropyridines using *n*-propylsilica kryptofix 21 and/or kryptofix 22-supported N₂O₄ (V or VI). *n*-Propylsilica kryptofix 21 (V, 0.45 g) or kryptofix 22-supported N₂O₄

Table 1

Rapid oxidation of urazoles **2** and 1,4-dihydropyridines **3** with *n*-propylsilica kryptofix 21 or kryptofix 22-supported N₂O₄ (V or VI) in CH₂Cl₂ at room temperature.

Entry	Substrate		Isolated yield (%)		Mp (°C) [10d]
	V	VI	V	VI	
1	2a	2a	100 ^a	100 ^a	98–99
2	2b	2b	100 ^a	100 ^a	54–55
3	2c	2c	91	90	41–43
4	2d	2d	90	87	42–43
5	2e	2e	90	86	96–97
6	2f	2f	82	78	172–175
7	2g	2g	80	75	122–124
8	2h	2h	82	78	180–183 (dec.)
9	2i	2i	70	67	125–126
10	2j	2j	90	85	110–112
11	2k	2k	87	85	132–135
12	2l	2l	87	83	90–93
13	3a	3a	91	98	71–72
14	3b	3b	85	80	Oil
15	3c	3c	88	86	62–63
16	3d	3d	84	82	61–62
17	3e	3e	83	81	113–115
18	3f	3f	90	87	56–58
19	3g	3g	76	70	37–39

^aConversion.

(VI, 0.5 g) was added to the solution of heterocyclic compounds (1 mmol) in CH₂Cl₂ (5 mL) and stirred at room temperature for 1–3 min. After the completion of the reaction, the reaction mixture was filtered and the CH₂Cl₂ removed to give the pure products.

Spectral and physical data for *n*-propylsilica kryptofix 21 or kryptofix 22 (III or IV). III: White powder, ir (KBr): 3445, 2350, 1548, 1096, 800, 465; XRD: 2θ = 9° (weak peak); 2θ = 21° (strong peak).

IV: White powder, ir (KBr): 3444, 2349, 1546, 1096, 802, 466. XRD: 2θ = 23° (strong peak).

Selected spectral and physical data for triazolinediones (4) [14] and pyridines (5) [14]. 4b (4-Ethyl-4H-1,2,4-triazol-3,5-dione): Pink crystals, Mp = 54–56°C, {Lit. [14a]: 54–55°C}, ¹H NMR (FT-90 MHz-deuteriochloroform): δ 1.32(t, 3H), 3.69 (q, 2H); ¹³C NMR (22.5 MHz-deuteriochloroform): δ 12.71, 36.7.

4c (4-*n*-Propyl-4H-1,2,4-triazol-3,5-dione): Pink crystals, Mp = 41–43°C, {Lit. [14a]: 44°C}, ¹H NMR (FT-90 MHz-deuteriochloroform): δ 0.94(t, 3H), 1.68(m, 2H), 3.63 (t, 2H); ¹³C NMR (22.5 MHz-deuteriochloroform): δ 10.66, 20.59, 42.88, 159.33.

4f (4-Phenyl-4H-1,2,4-triazol-3,5-dione): Red crystals, Mp = 172–175°C, {Lit. [14a]: 171–175°C}, ¹H NMR (FT-90 MHz-deuteriochloroform): δ 7.48 (s); ¹³C NMR (22.5 MHz-deuteriochloroform): δ 124.2, 129.01, 129.9, 157.971.

5c (Diethyl 2,6-dimethyl-4-phenylpyridine-3,5-dicarboxylate): Pale yellow crystals, Mp = 62–63°C, {Lit. [10d]: 62–64°C}, ¹H NMR (FT-90 MHz-deuteriochloroform): δ 1.23 (t, 6H), 2.63 (s, 6H), 4.27 (q, 4H), 7.2–7.5(m, 5H); ir (KBr): 1254, 1377, 1456, 1688, 1733, 2854.

5d [Diethyl 2,6-dimethyl-4-(3-nitrophenyl)pyridine-3,5-dicarboxylate]: Pale yellow crystals Mp = 61–63°C, {Lit. [10d]: 61–62°C}, ¹H NMR (FT-90 MHz-deuteriochloroform): δ 1.29 (t, 6H), 2.55 (s, 6H), 4.31 (q, 4H), 7.4–7.7 (m, 4H); ir (KBr): 1038, 1248, 1362, 1462, 1531, 1729, 2854.

In conclusion, *n*-propylsilica kryptofix 21 or kriptofix 22-supported N₂O₄ (V or VI) are two new safe and easy-handling N₂O₄-polymer-supported reagents. They can act as unique powerful system for the fast oxidation of urazoles and dihydropyridines under heterogeneous, metal free, and mild conditions *via in situ* generation of NO⁺ without water. Reaction procedure offer advantages such as simple work-up, very low reaction times, good to excellent yields, and matching with green chemistry protocols.

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