




RAPID COMMUNICATION

Nickel-catalyzed direct synthesis of dialkoxymethane ethers[†]

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MS received 16 May 2017; revised 4 July 2017; accepted 5 July 2017

Abstract. A simple and efficient method for the preparation of dialkoxymethane ethers (oxymethylene ethers) from alcohols and paraformaldehyde in the presence of commercially available nickel(II) salt is described. The reaction proceeds readily under neutral, solvent-free conditions using paraformaldehyde as a C₁ source. The present strategy has a broad substrate scope including aliphatic (both primary and secondary) and aromatic alcohols and provides a benign method for the preparation of symmetrical dialkoxymethanes in good yields (up to 89%).

Keywords. Nickel catalysis; alcohol; paraformaldehyde; ether; solvent-free condition.

1. Introduction

Ethers constitute the most diverse family of organic compounds and are ubiquitous in many natural products and pharmaceuticals.¹ The extent to which they can be utilized as an organic intermediate in contemporary science depends on the selectivity and efficiency of the processes for their preparation from simple feedstock chemicals. Consequently, there are various synthetic routes that have been documented to access symmetrical as well as unsymmetrical ethers, ranging from the classical Williamson ether synthesis² to recent transition-metal catalyzed cross-coupling reactions employing alcohols.³

In recent years, the dialkoxymethane (oxymethylene ether) has been gaining increasing interest because of its advantageous properties as fuel additives for combustion engines (e.g., dimethoxymethane, DMM).⁴ Further various biologically significant compounds, for example, Miloxacin (antibacterial agent)⁵ and Cephalotaxine (antiviral and antitumor agent)⁶ contain the dialkoxymethane motif. The dialkoxymethane and its derivatives

have been used as a source for the synthesis of plasticizers, and monomers for cross-linking agents.⁷ In addition, they have been used as an intermediate for the preparation of drug-related compounds such as anti-HIV-1 drug (TNK-651),⁸ microbicidally active drug (YML-220) for infected MT-4 cells,⁹ portmanteau inhibitors against reverse transcriptase (RT), and the inhibitor of HIV-1 Integrase (IN), etc.^{10,11} The use of dialkoxymethane as reagents for the *N*-alkoxymethylation of secondary amides in the presence of Lewis acids¹² and Brønsted acids¹³ has also been reported. Given their importance, the development of efficient, benign strategies for the synthesis of dialkoxymethane is a central research area in synthetic chemistry (Figure 1).

The general strategy for the preparation of dialkoxymethanes involves the condensation reaction of toxic formaldehyde with alcohols under acidic conditions.^{9,14,15} Several methods including NaH/dibromomethane,⁹ montmorillonite/dichloromethane in NaOH/H₂O mixture,^{14c} Me₃SiCl/Me₂SO^{14a} with alcohol have been reported. The Cu-NHC-catalyzed

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[†] Dedicated to Professor K. C. Kumara Swamy on the occasion of his 60th birth anniversary.

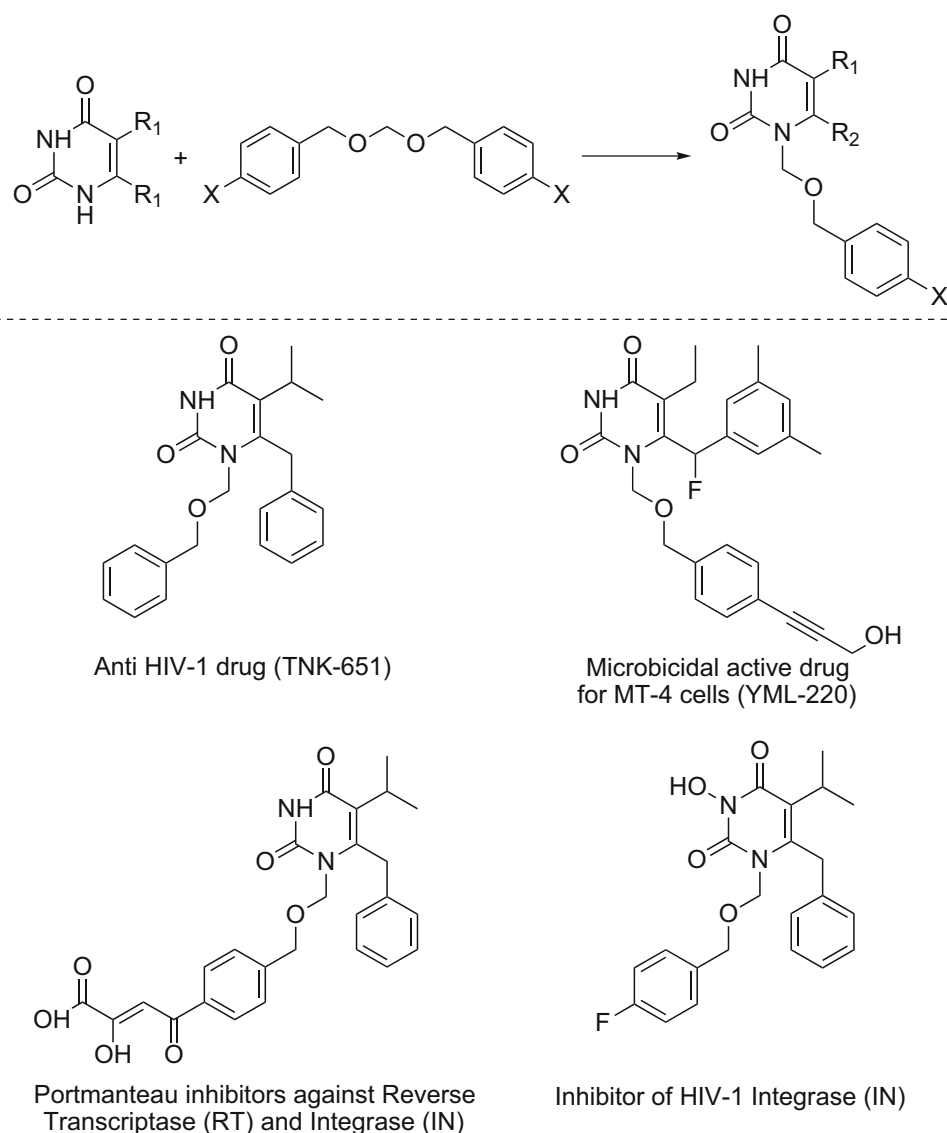
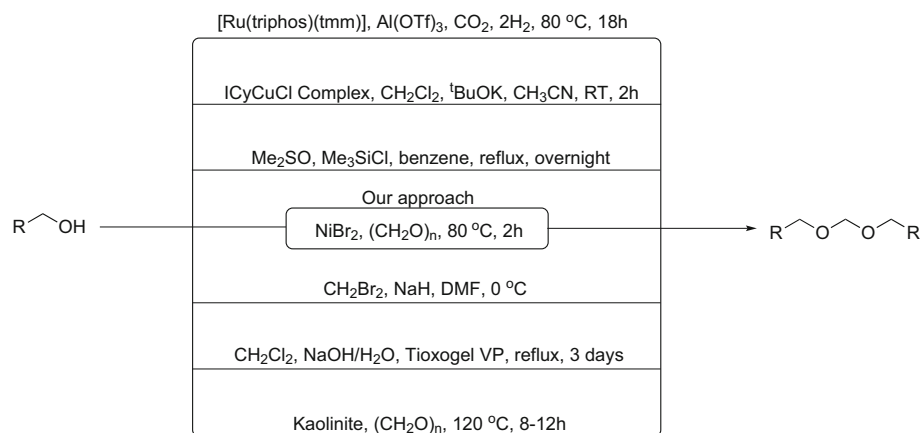


Figure 1. Dialkoxymethane as intermediates in the synthesis of drug-related molecules.

preparation of dialkoxymethanes from dichloromethane with alcohols has been reported by Zhan *et al.*^{14j} A heterogeneous Kaolinite (a clay mineral of alumina and silica) catalyzed preparation of dialkoxymethanes using paraformaldehyde has also been reported; however, it requires high temperature and a long reaction time.^{14e} Very recently, Klankermayer *et al.*, demonstrated the catalytic conversion of CO₂ (20 bar) and H₂ (60 bar) in the presence of alcohols into dialkoxymethane ethers in a multistep reaction using a well-defined ruthenium-triphos catalyst and aluminium triflate as a Lewis acidic co-catalyst. The achieved turnover numbers were about 200 TONs for methanol and varied from 50 to 120 TONs for the higher aliphatic alcohols.¹⁶ However, most of these methods suffer from several disadvantages such as (i) the use of a stoichiometric amount of hazardous halogenated reagents

resulting in copious waste, (ii) operate under acidic or basic conditions and elevated reaction temperature (~120°C), (iii) require longer reaction times, and (iv) often take place in harmful organic solvents.¹⁴ Hence, it would be appealing to develop a mild and environmentally benign synthesis of dialkoxymethane ethers under neutral conditions and to avoid the use of toxic organic solvents. Here, we report a simple, efficient method for the preparation of dialkoxymethanes from alcohols and paraformaldehyde (which is cheap and stable at ambient conditions as well as exhibits low-toxicity; for selected examples of paraformaldehyde used as a C-1 source),¹⁷ in the presence of a commercially available nickel(II) salt. The reaction proceeds readily under mild, neutral and solvent-free conditions in a short period of reaction time. To the best of our knowledge, there are no reports that describe



Scheme 1. Various strategies for the preparation of dialkoxymethanes.

the nickel-catalyzed synthesis of dialkoxymethanes (Scheme 1).

2. Experimental

2.1 Materials and methods

All catalytic experiments were carried out using standard Schlenk techniques. The reagents and solvents used were chemically pure and analytical grade, and the solvents were dried according to standard procedures. Alcohols were distilled under vacuum. Nickel salts (purchased from Sigma-Aldrich) and paraformaldehyde were used without additional purification. Column chromatography was performed with SiO₂ (Silicycle Siliaflash F60 (230-400 mesh)). ¹H NMR (200, 400 or 500 MHz), ¹³C{¹H} NMR (50 or 100 MHz) spectra were recorded on the NMR spectrometer. Deuterated chloroform was used as the solvent, and chemical shift values (δ) are reported in parts per million relative to the residual signals of this solvent [δ 7.26 for ¹H (chloroform-d), δ 77.2 for ¹³C{¹H} (chloroform-d)]. Abbreviations used in the NMR follow-up experiments are as follows: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. GC analysis was carried out using an HP-5 column (30 m, 0.25 mm, 0.25 μ m). Mass spectra were obtained on a GCMS-QP 5000 instruments with ionization voltages of 70 eV. High-resolution mass spectra (HRMS) were obtained by fast atom bombardment (FAB) using a double focusing magnetic sector mass spectrometer and electron impact (EI) ionization technique (magnetic sector-electric sector double focusing mass analyzer).

2.2 Synthesis of Ni-Octane thiolate

To 500 mg of nickel(II) acetylacetonate (or nickel(II)acetate) taken in an eppendorf tube of 2 mL capacity, 900 μ L of octanethiol was added and the tube was shaken vigorously. The reaction mixture turned black instantaneously. The mixture was washed thoroughly with ethanol, and the black product was air-dried at room temperature. The obtained black

powder goes readily into organic solvents such as chloroform, toluene, CCl₄, etc. The powder was characterized using PXRD and TEM analysis and the data is consistent with the literature compound.¹⁸

2.3 Synthesis of Ni₃S₂ Sheets

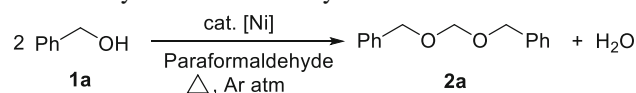
Nickel octanethiolate powder sample was heated in a tube-furnace equipped with Argon gas flow maintaining a constant temperature of 750°C and at a constant gas flow rate of 2 mL/sec for 6 h. After heating for 6 h, the sample was cooled to room temperature and the final product was collected and characterized by PXRD and TEM (see Supporting Information).

2.4 General procedure for the preparation of dialkoxymethane ethers from alcohols

In an oven-dried screw cap reaction tube (15 mL), alcohol (0.5 mmol), paraformaldehyde (1 mmol) and NiBr₂ (5 mol%) were added under a gentle stream of argon. The reaction mixture was stirred at 80°C in an oil bath for 2 h. After completion of the reaction, the mixture was allowed to cool at room temperature, and the reaction was subsequently quenched with water (10 mL) followed by the extraction with ethyl acetate (3 \times 10 mL). The organic layer was separated and dried over anhydrous Na₂SO₄. Evaporation of the solvent under reduced pressure gave the crude product, which was chromatographed on silica gel using pet. ether and EtOAc (98:2) as an eluent to afford the desired dialkoxymethanes. All the compounds were completely characterized, and the spectroscopic data with copies of spectra are provided in the Supporting Information.

2.5 Homogeneity test

An alcohol (0.5 mmol), paraformaldehyde (1 mmol), NiBr₂ (5 mol%), and one drop of mercury were taken in a round-bottom flask and stirred at 80°C temperature. After 2 h, the reaction mixture was allowed to cool to room temperature. The reaction products were analyzed with gas chromatography using *m*-xylene as an internal standard, and the product were confirmed by GC-MS.

Table 1. Optimization condition for the synthesis of dialkoxymethanes^a.

Entry	Nickel catalyst	Solvent	Temp (°C)	Yield of 2a (%) ^b
1	Ni-Octane thiolate	—	80°C	41
2	Ni ₃ S ₂ nano-sheet	—	80°C	14
3	NiBr ₂	—	80°C	80 (71) ^c
4	NiBr ₂ + DPPE	—	80°C	24
5	NiBr ₂ + BPy	—	80°C	11
6	NiBr ₂ + Pyridine	—	80°C	Trace
7	—	—	80°C	n.d
8	NiCl ₂	—	80°C	67 ^b
9	Ni(acac) ₂	—	80°C	n.d
10	NiCp ₂	—	80°C	n.d
11	Ni(OAc) ₂	—	80°C	23
12	Ni[PPh ₃] ₄	—	80°C	n.d
13	NiBr ₂	Toluene	80°C	n.d
14	NiBr ₂	Acetonitrile	80°C	Trace
15	NiBr ₂	THF	80°C	Trace
16	NiBr ₂	—	rt	n.d
17	NiBr ₂	—	50°C	26
18	NiBr ₂	—	110°C	67
19	NiBr ₂ + Hg	—	80°C	70

^aReaction condition: Benzyl alcohol **1a** (0.5 mmol), (HCHO)_n (1.0 mmol), cat.[Ni] (5 mol%), heated at 80°C in an oil bath for 2 h under argon atm (entries 3–19).

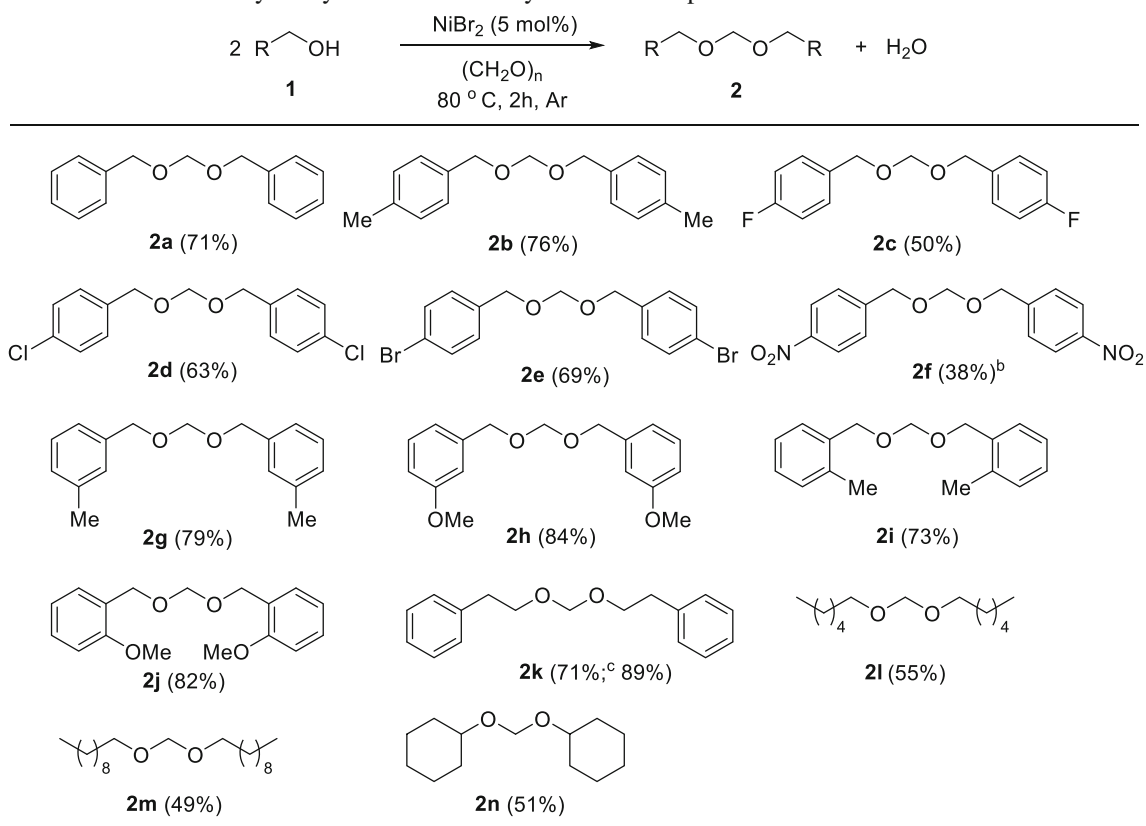
^bYields were determined by GC using *m*-xylene as an internal standard.

^cIsolated yields. *n.d* not detected.

3. Results and Discussion

Nickel based catalysts have gained significant attention in sustainable chemical synthesis owing to the Nickel abundance, economical and versatile reactivity.¹⁹ Optimization studies on the nickel-catalyzed direct synthesis of dialkoxymethane ethers are summarized in Table 1. Initially, the catalytic activity of Ni-Octane thiolate was tested using benzyl alcohol (**1a**) as a model substrate and paraformaldehyde as a C-1 source. Thus, treatment of benzyl alcohol (0.5 mmol) with paraformaldehyde (1 mmol) at 80°C for 8 h with a catalytic amount of Ni-Octane thiolate under *solvent-free* conditions, resulted in 41% of bis(benzyloxy)methane **2a** (Table 1, entry 1). Under identical conditions Ni₃S₂ nano-sheets (after pyrolysis of Ni-Octane thiolate at 750°C) gave only 14% of the desired product (Table 1, entry 2). Encouraged by these preliminary results, next we have examined several nickel catalysts for this transformation. Notably, with NiBr₂ (5 mol%), the reaction of benzyl alcohol with paraformaldehyde at 80°C in an oil bath for 2 h resulted 71% isolated yield of **2a** (Table 1, entry 3). Next, the activity of *in situ* generated nickel complexes (L_nNi) was studied. In this regard, a series of monodentate (PPh₃ and (*o*-Tolyl)₃P) and bidentate

ligands (phosphine and nitrogen-based ligands) were tested using nickel(II) bromide as the catalyst precursor (Table 1, entries 4–6). However, almost all of the ligands we examined gave quite low catalytic activity with less than 25% yield of the desired product **2a**. Next, we have investigated the impact of key reaction parameters for the desired transformation. The effect of different nickel catalyst precursors was also explored, and other nickel(II) and nickel(0) catalysts showed less reactivity under regular conditions (Table 1, entries 8–12). Using 2 mol% of NiBr₂ under the regular conditions, **2a** was obtained in 65% yield and no reaction was observed in the absence of nickel(II) bromide (Table 1, entry 7). The solvent dependency of the same reaction was carried out (Table 1, entries 13–15). Notably, an excess of paraformaldehyde inhibited this transformation. Thus, using 5 eq. of paraformaldehyde under optimized reaction conditions gave only 21% of **2a**. By lowering the temperature, we obtained the product in lower yield (Table 1, entries 16–18) and formation of **2a** was not observed at room temperature. An increase of the reaction time did not increase the yield of the product significantly. Indeed, the mercury poisoning experiment indicates the homogeneous nature of the present nickel catalysis systems (Table 1, entry 19). Gratifyingly, these

Table 2. Nickel-catalyzed synthesis of dialkoxymethanes: scope of alcohols^a.

^aReaction condition: Alcohol **1** (0.5 mmol), (HCHO)_n (1.0 mmol), NiBr₂ (5 mol%), heated at 80°C in an oil bath for 2 h; isolated yields are given in the parenthesis.

^bBased on GC analysis using *m*-xylene as an internal standard.

^c2 mol% of NiBr₂.

optimal conditions employed a readily available nickel catalyst and paraformaldehyde as C1-source and proceeded readily at a moderate temperature under neutral conditions with the generation of water as the sole by-product. Indeed, the *solvent-free* condition was regarded as the best for the cost and ecological benefits. This representative transformation helps to manifest the practical value that this method may offer for rapid and reliable access of dialkoxymethanes under very mild, eco-benign conditions.

With an optimized the catalytic system in hand (Table 1), next, we have studied the versatility of this new approach towards the synthesis of dialkoxymethanes. As shown in Table 2, the developed strategy is general and compatible with various alcohols including aliphatic (both primary and secondary) and aromatic alcohols and provides a benign method for the preparation of symmetrical dialkoxymethanes in good yields with a shorter reaction time. In general, benzyl alcohol containing no substituents and electron-donating substituents were found to proceed with higher yields than those with electron-withdrawing substituents (-NO₂ and

-F) under optimized reaction conditions. The reason would be that in presence of an electron-donating group like methoxy at *ortho* and *para* positions increases the electron density and thus facilitates the insertion reaction with the nickel complex. Indeed, reactions with various *ortho*-, *meta*-, and *para*-substituted benzyl alcohols proceeded smoothly under our optimized conditions and gave the desired product in moderate to good yields. Aliphatic primary and alicyclic secondary alcohols were also well tolerated for this transformation and gave the desired products in moderate yields (product **2l** in 55%, **2m** in 49% and **2n** in 51% isolated yields).

4. Conclusions

In conclusion, a facile nickel-catalyzed synthesis of dialkoxymethanes under neutral conditions is reported using cheap, commercially available NiBr₂. Employing this readily available nickel catalyst and paraformaldehyde as C1-source, a variety of alcohols with wide

substrate scope (aliphatic primary and secondary, and aromatic alcohols) were efficiently converted into dialkoxymethanes in moderate to good yields (up to 89%) under benign conditions. Solvent-free conditions, moderate temperature, shorter reaction times, and economic viability of the catalyst are the key features of the present protocol.

Supplementary Information (SI)

Full characterization details, copies of NMR (¹H and ¹³C NMR) spectra, HRMS data for all the compounds are presented in Supplementary Information, which is available at www.ias.ac.in/chemsci.

Acknowledgements

This research was supported by the SERB (SB/FT/CS-065/2013). MS and AB thank UGC, India for the research fellowships. BLVP acknowledges the Council of Scientific and Industrial Research, India for the financial support through the project CSC0134.

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