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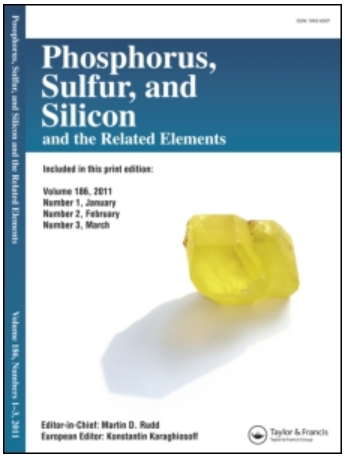

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CaS_2O_8: An Efficient Reagent for Etherification of Alcohols under Microwave Irradiation in Solvent-Free Conditions

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To cite this Article Badri, Rashid , Kiasat, Ali Reza and Nazari, Simin(2007) 'CaS_2O_8: An Efficient Reagent for Etherification of Alcohols under Microwave Irradiation in Solvent-Free Conditions', Phosphorus, Sulfur, and Silicon and the Related Elements, 182: 3, 589 — 593
To link to this Article: DOI: 10.1080/10426500601015682
URL: http://dx.doi.org/10.1080/10426500601015682

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Phosphorus, Sulfur, and Silicon, 182:589–593, 2007
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500601015682

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CaS_2O_8: An Efficient Reagent for Etherification of Alcohols under Microwave Irradiation in Solvent-Free Conditions

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A new facile and efficient one-pot method for the synthesis of ethers by the reaction of alcohols with calcium peroxodisulfate under microwave irradiation is described.

Keywords Alcohols; calcium peroxodisulfate; microwave irradiation; solvent free; symmetrical ethers

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Etherification is one of the most frequently used functional-group transformations in organic synthesis.[1] The most common method to produce ethers is the Williamson synthesis,[2] which involves the reaction of an alkyl halide and a basic alkoxide. However, base-labile functionalities in reactants and competing eliminations in the case of secondary and tertiary halides restrict its application to a wide range of substrates. In addition, the dehydration of alcohols, especially primary alcohols, is the common method for the preparation of symmetrical ethers.[3] This condensation reaction is catalyzed by strong acids such as sulphuric acid at elevated temperatures. Recently, the application of solid acids such as ion-exchange resins, zeolites, and aluminum phosphates was reported for the synthesis of symmetrical ethers.[4–6]

Although the use of the peroxodisulfate anion ($S_2O_8^{2-}$) as a strong one-electron transfer oxidant for the oxidation of a variety of organic compounds has been under intensive investigations in recent years,[7–10] its application for the protection of alcohols as tetrahydropyranyl ethers was reported.[11] To the best of our knowledge, no report about the use

Received August 4, 2005; accepted August 16, 2006.
We thank Shahid, Chamran University, Ahvaz, Iran for financial support of this work.
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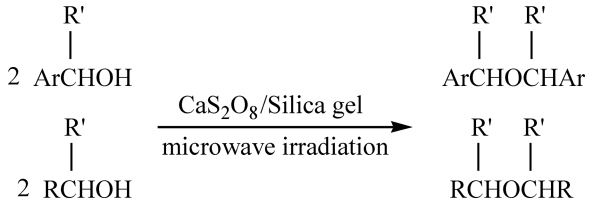
of the peroxodisulfate anion for the conversion of different alcohols to corresponding ethers has been reported.

In previous articles we reported the use of peroxodisulfate anion as an efficient oxidant for the conversion of alcohols, alkyl benzenes, and certain benzylic substrates to their corresponding carbonyl compounds.[12–14] Here we report a convenient synthesis of various types of symmetrical ethers from corresponding primary and secondary alcohols under microwave irradiation and under solvent-free conditions using calcium peroxodisulfate (Scheme 1).



SCHEME 1

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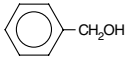
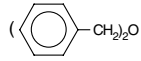
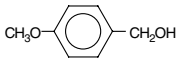
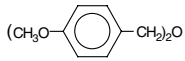
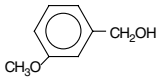
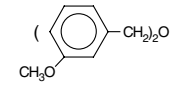
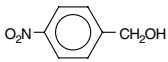
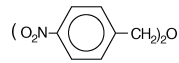
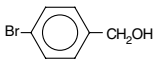
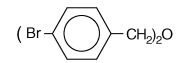
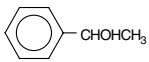
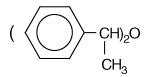
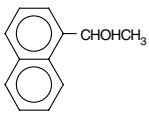
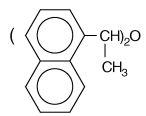
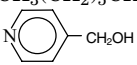
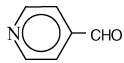
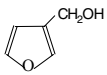
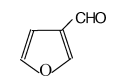
The starting point was the reagent CaS_2O_8, which can be conveniently prepared from calcium oxide and ammonium peroxodisulfate in water. This reagent was then mixed with silica gel and an alcohol and irradiated in a microwave oven for an appropriate time. The ethers prepared in this investigation and their yields are listed in Table I.

As shown in Table I, various types of alcohols react efficiently with calcium peroxodisulfate to afford corresponding ethers in good to excellent yields. Primary and secondary benzylic alcohols proved to be more efficient and gave higher yields than aliphatic and non-benzylic alcohols (Table I). Since some heterocyclic alcohols instead of giving ethers were converted to corresponding carbonyl compounds (Table I), we suspect that oxidation of alcohols to their carbonyl derivatives might happen initially followed by the transformation of these carbonyl compounds to ethers during the reaction course. In order to eliminate the ambiguity of intermediacy of carbonyl compounds during ether formation, we tried syntheses under the same reaction conditions and time with a mixture of equimolar amounts of alcohol and its corresponding aldehyde or ketone. No conversion of the carbonyl compound to the ether was observed, and the isolated products from the reaction mixture were the corresponding ether resulting from alcohol and the unreacted carbonyl compound. This evidence clearly rejects the possible intermediacy of carbonyl compounds in the conversion of alcohols to ethers.

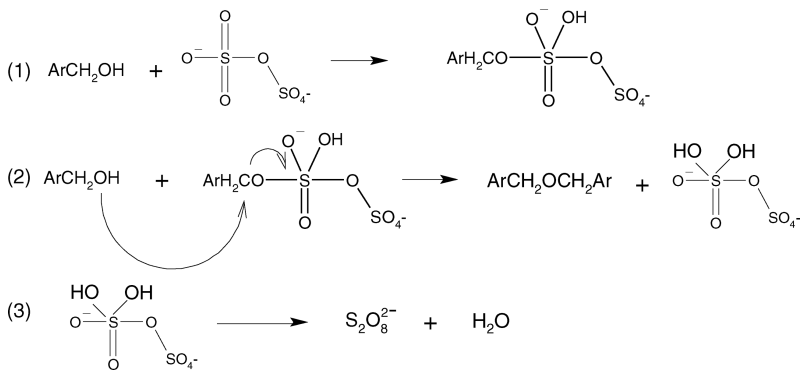
A plausible mechanism could be as showin in Scheme 2.

TABLE I Conversion of Alcohols to Symmetrical Ethers by CaS_2O_8 Under Microwave Irradiation Under Solvent–Free Conditions

Substrate	Product	Time (min)	Yield[a,b] (%)
		4	81
		7	95
		8	80
		10	85
		8	92
		6	83
		6	85
$CH_3(CH_2)_6CH_2OH$	$(CH_3(CH_2)_6CH_2)_2O$	5	71
$CH_3(CH_2)_5CHOHCH_3$		5	78
		5	91
		5	90

[a]Yields refer to pure isolated products.

[b]Products were characterized by comparison of their physical data, and IR and ^1H NMR spectra with those of authentic samples.



SCHEME 2

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CONCLUSION

The procedure for the synthesis of ethers described in this article has the advantage of simple reaction conditions, easy work-up, and excellent yields. It provides an attractive alternate method for the preparation of ethers.

EXPERIMENTAL

General

^{1}H NMR spectra were recorded on a Bruker Advance DPX instrument (250 MHz). IR spectra were recorded on a Shimadzu 470 spectrophotometer. Melting points were measured on a Mettler FP5 apparatus. Purity determination of the products and reaction monitoring were accomplished by TLC on silica gel polygram SILG/UV254 plates. All yields refer to isolated products. Reactions were performed in a microwave oven with a 230V-50 Hz power source, 900 W output, and 2450 MHz operating frequency.

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General Procedure for the Synthesis of CaS_2O_8

To a solution of calcium oxide (1.12 g, 20 mmol) in water (25 mL) in a round-bottomed flask equipped with a magnetic stirrer was added ammonium peroxodisulfate (4.5 g, 20 mmol). The reaction mixture was stirred at an ambient temperature for 2 h, and then neutral silica gel (10 g) was added. Stirring was continued for an additional 2 h, after which the water was removed. The white solid was dried and used for the synthesis of ethers.

General Procedure for the Synthesis of Ethers

In a 100-mL glass beaker, alcohol (1 mmol), calcium peroxodisufate (2 mmol), and 2 drops of water were mixed thoroughly; the mixture was placed in a microwave oven and irradiated at 30% power level for an appropriate time (4–10 min). After cooling, chloroform (20–30 mL) was added, and the mixture was stirred for 45 min and filtered. The solid material was washed with chloroform (20 mL), the solvent from the filtrate was evaporated, and the crude product was purified on a silica gel plate (eluent: CCl_4/Et_2O 4/1). Pure ethers were obtained in 71–95% yields (Table I).

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