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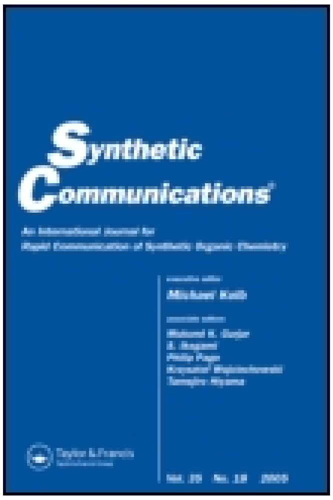

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MICROWAVE-ASSISTED ACETALIZATION OF PENTAERYTHRITOL CATALYZED BY 12-TUNGSTOPHOSPHORIC ACID

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MICROWAVE-ASSISTED ACETALIZATION OF PENTAERYTHRITOL CATALYZED BY 12-TUNGSTOPHOSPHORIC ACID

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ABSTRACT

Efficient conversion of carbonyl compounds and pentaerythritol to corresponding diacetals in the presence of 12-tungstophosphoric acid under microwave irradiation is described.

The diacetals of pentaerythritol are a series of useful organic compounds.[1] They have been used as plasticizers and vulcanizers, as physiologically active substance, and as potential protective groups in organic synthesis. The preparation of these compounds has been well investigated. A variety of acidic catalysts, such as hydrochloric acid, sulfuric acid, *p*-toluenesulfonic acid,[1] zinc chloride,[2] acidic cation exchanger,[3] Montmorillonite clay,[4] expansive graphite[5] and anhydrous ferrous sulfate[6] have been used for this purpose.

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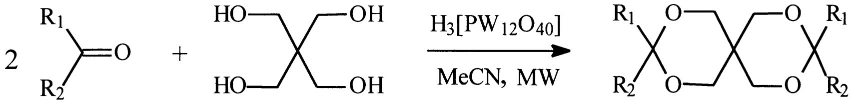
Microwave dielectric heating has become an important technique in organic synthesis.[7] Wang et al. have presented their method by which the diacetals of pentaerythritol were prepared in the presence of *p*-toluenesulfonic acid in a domestic microwave oven.[8] We report herein a rapid and facile procedure for the synthesis of pentaerythritol diacetals under microwave irradiation catalyzed by 12-tungstophosphoric acid[9] (Scheme 1). Up to now, there is no report of the use of heteropolyacids as catalysts in microwave-prompted organic reactions. The 12-tungstophosphoric acid showed excellent activity in the acetalization reaction, hence, the amount of catalyst used here (molar ratio of catalyst to substrate = 1/200) is much less than that in the reported process (the molar ratio of catalyst to substrate = 1/36).[8]

In experiment, carbonyl compounds were treated with 0.5 equivalent of pentaerythritol in the presence of 12-tungstophosphoric acid under microwave irradiation leading to diacetals in satisfactory yields, except for benzophenone. Acetonitrile was used as solvent because of its high dielectric constant and outstanding solubility. The results are summarized in the table.



Scheme 1.

Table. Microwave-Assisted Acetalization of Pentaerythritol

Entry	Carbonyl Compounds	Power (W)	Time (min)	Yield[a] (%)	M.P. (°C) Found[b]	M.P. (°C) Lit.
1	Benzaldehyde	300	8	80	159–160	155–156[8]
2	4-Chlorobenzaldehyde	400	2	90	199–200	197–198[8]
3	2,4-Dichlorobenzaldehyde	400	6	81	180–181	178–180[8]
4	3-Nitrobenzaldehyde	400	5	93	180–182	179–180[8]
5	4-Hydroxybenzaldehyde	400	5	72	111–112	109–110[8]
6	Vanillin	400	5	78	171–172	170–171[4]
7	Cinnamaldehyde	300	2	66	196–198	195[10]
8	Cyclohexanone	400	12	67	115–116	113–114[4]
9	Cyclopentanone	400	12	62	154–155	153–154[2]
10	Benzophenone	400	12	0	–	–

[a]Isolated yield; [b]Recrystallization from *n*-butanol.

The acetalization of both aldehydes and ketones have been investigated. In many cases (except for 4-hydroxybenzaldehyde), our protocol gave shorter reaction time and higher yields than presented literature.[8] Aromatic aldehydes with strong electron-donor groups, such as hydroxy, show less reactivity and give lower yields. Cinnamaldehyde with pentaerythritol for 2 min at 300 W microwave irradiation afforded a moderate yield (66%) of the corresponding diacetals. Prolonged reaction time and higher microwave power level resulted in dark-brown polymeric by-products. Ketones show less reactivity than aldehydes. Benzophenone failed to give the desired diacetal under above reaction conditions perhaps due to higher steric hindrance.

In conclusion, this process for the synthesis of pentaerythritol diacetals is rapid, convenient and provides products in high yields with simple work-up procedure.

EXPERIMENTAL SECTION

Melting points (uncorrected) were taking in open capillary on a WRS-1 digital melting point apparatus manufactured in Shanghai. IR spectra were recorded as KBr pellets on a Model 7650 spectrometer. All reagents were commercially available and used without purification. Reactions were conducted in a MW-800 II multimode cavity refluxing system made by Microwave Research Center of East China Normal University.

Typical procedure. A solution of 4-chlorobenzaldehyde (2.81 g, 20 mmol), pentaerythritol (1.36 g, 10 mmol), 12-tungstophosphoric acid (0.33 g, 0.1 mmol) in acetonitrile (20 mL) is refluxed during 2 min under microwave irradiation. The solvent was evaporated *in vacuo* and the residue was washed with hot water. Recrystallization from *n*-butanol gave 3.44 g (90% yield) of corresponding diacetal as white needles. Mp 199–200°C (Lit.[8] 197–198°C).

IR (KBr, cm^{-1}): 2860, 1600, 1495, 1385, 1340, 1205, 1170, 1080, 815.

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