(1H, d, J=3.5 Hz, anomeric-H); ^{13}C-NMR (75 MHz, CD_3OD, δc) of fatty acid moiety: 175.6(s), 34.9(t), 33.0(t), 30.7 (t), 30.6(t), 30.4(t), 30.2(t), 25.9(t), 23.7(t), 14.4(q).

10. **4**; $[\alpha]_D$+51°(c 0.6, H_2O); SIMS (m/z): 363 $[M+Na]^+$, 703 $[2M+Na]^+$; ^{1}H-NMR(300 MHz, D_2O, δ): 3.08(1H, dd, J=14.5, 10.0 Hz), 3.27(1H, dd, J=9.5, 9.0 Hz), 3.36(1H, d, J=4.5 Hz), 3.42-3.49(1H, m), 3.57-3.63(2H, m), 3.68-3.78 (2H, m), 3.93-4.06(3H, m), 4.90(1H, d, J=3.5 Hz, anomeric-H); ^{13}C-NMR (75 MHz, D_2O, δc): see Table 1, and B.-W. Son, *Phytochemistry*, **29**, 307 (1990).
11. Analytical conditions for GC and GC-MS were the same as described in that of a mixture of fatty acid methyl esters of **1**,[8] [t_R(min.)=**b** 5'57", **c** 10'40"; **b** : **c**=96 : 4].
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A Convenient Method for the Formation of *p*-Methoxylbenzyl Ethers and Esters over Perfluorinated Resinsulfonic Acid (Nafion-H)

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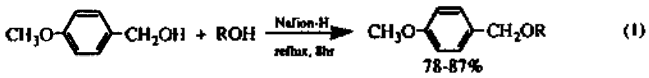
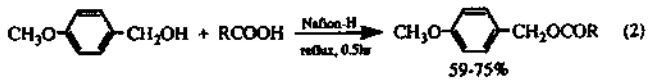
Nafion-H (a solid perfluorinated resinsulfonic acid having sulfonic acid group in the amount of 0.01 to 5 mequiv/gram resin)[1-3] has been used as an efficient catalyst in a number of acid catalyzed reactions.[4-7] Earlier we described convenient methods for esterification and benzylation over Nafion-H catalyst.[8,9] The esterification reactions between alkyl alcohols with carboxylicc acids proceeded cleanly to afford the desired products in nearly quantitative yields. Similarly, benzyl alcohol reacted readily with arenes to produce the benzylated products in excellent yields. However, benzyl alcohol did not react with alkyl alcohols and produced polymeric material when reacted with carboxylic acids. We now report that *p*-methoxybenzyl alcohol reacts readily with alcohols and carboxylic acids in the presence of catalytic amount of Nafion-H to afford *p*-methoxybenzyl ethers and esters, which have been prepared by different methods and used as protecting groups for alcohols and carboxylic acids.[10] (Eq 1 & 2)



(1)



(2)

The reaction was carried out by refluxing a mixture of *p*-methoxybenzyl alcohol (1.0 g), alkyl alcohol (5.0 m*l*), and Nafion-H (0.2 g) for 8 hours. Water was removed with small amount of silica gel in a soxhlet thimble suspended just below refluxing condenser. The product were simply isolated by filtering the hot reaction mixture and distilling off the excess alcohol. The results are summarized in Table 1. The reactions are very clean and produce the desired ethers in high yields. The esterification reactions of *p*-methoxybenzyl alcohol with carboxylic acids were conducted either by refluxing the reaction mixture for 30 min or by stirring the mixture for 8 hrs at room temperature to produce the *p*-methoxybenzyl esters in moderate to excellent yields (Table 2).

Table 1. Yield of Reaction between *p*-Methoxybenzy Alcohol and Alcohols (ROH) Catalyzed by Nafion-H

R	Yield (%)[a]	bp/mmHg	lit.[b] bp/mmHg
CH_3	86.5	66-8/1.5	102- 3/9
C_2H_5	78.4	90-4/2.3	109-10/9
C_3H_7	84.2	83-4/1.5	127- 8/11
C_4H_9	78.4	94-6/1.5	134- 5/10

[a]Isolated yield after reflux for 8 hrs, [b]Reference 11.

Table 2. Yield of Reactions Between *p*-Methoxybenzyl Alcohol and Carboxylic Acids (ROOH) Catalyzed by Nafion-H

R	Yield (%)[a]	bp/mmHg	lit.[b] bp/mmHg
CH_3	72.3(100)[b]	95-7/1.4	137-9/12[c]
C_2H_5	75.4(90.9)[b]	94-9/1.4	d
C_3H_7	58.7(74.6)[b]	102-7/1.4	158-68/11[c]
C_4H_9	60.0(52.9)[b]	99-103/1.5	d

[a]Isolated yield after reflux for 0.5 hour, [b]G.C. yield after 8 hrs at room temperature, [c]Reference 12, [d]Identified by NMR and IR.

The remarkable difference in reactivity between benzyl alcohol and its *p*-methoxy derivative can be attributed to the substituent effect. *p*-Methoxybenzyl cation should be more stable than benzyl cation and thus should exist in higher concentration than the latter. Although the former should be less reactive than the latter, the difference in reactivity between these two electrophiles is not expected to be as great as that of their concentration because the reactions between the benzylic cations and the oxygen nucleophiles must be highly exothermic. Therefore, it is reasonble to expect that the former should react faster than the latter with alcohols and carboxylic acids. The faster rate of ester formation may be attributed to the participation of the carboxylic acids as a catalyst in these reactions.

The present procedure provides an efficient method for the formation of *p*-methoxybenzyl ethers and esters. In this procedure, only a catalytic amount of the acidic resin is needed, and the heterogeneous catalyst provides for a very simple work-up. Application of Nafion-H on other acid catalyzed reactions are in progress in our laboratory.

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