

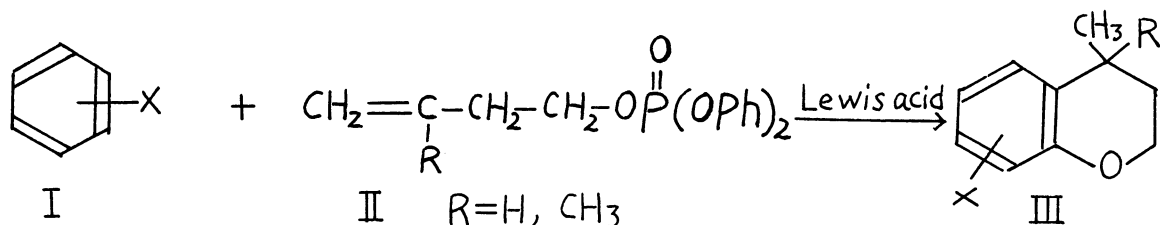
ONE-STEP SYNTHESIS OF 4-METHYLCHROMANS FROM PHENOL DERIVATIVES
AND 3-BUTENYL OR 3-METHYL-3-BUTENYL DIPHENYL PHOSPHATE

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3-Butenyl or 3-methyl-3-butenyl diphenyl phosphate reacted with phenols or phenyl ethers in the presence of a Lewis acid under mild conditions to give selectively 4-methyl or 4,4-dimethylchromans in 10-53% yields.

4-Methyl or 4,4-dimethylchromans have been synthesized by the reduction of 4-methyl or 4,4-dimethylhydrocoumarins, followed by the dehydration of the corresponding diols;^{1),2),3),4)} or by the Grignard reaction of 4-chromanones with methylmagnesium bromide, followed by the hydrogenation of the corresponding 4-methyl-4-chromanols.⁵⁾ However, these methods need multi-steps.

We wish to report a one-step synthesis of 4-methyl and 4,4-dimethylchromans in 10-53% yield by the reaction of 1-5 molar equivalents of phenol derivatives with 3-butenyl or 3-methyl-3-butenyl diphenyl phosphate in the presence of a Lewis acid at room temperature. Thus, 3-butenyl or 3-methyl-3-butenyl diphenyl phosphate was added to a mixture of a phenol derivative and a Lewis acid at room temperature, and the mixture was stirred for 5 hr. The reaction was quenched by addition of ice water and the products were extracted with ether. They were separated by vacuum-distillation and subsequent preparative g.l.c.. The results are shown in Table.



It should be noted that 3-butenyl diphenyl phosphate did not react with phenol derivatives in the presence of boron trifluoride etherate or stannic chloride under the conditions, but reacted in the presence of aluminium chloride to give exclusively 4-methylchromans. On the other hand, 3-methyl-3-butenyl diphenyl phosphate reacted more or less with phenol derivatives in the presence of any of these Lewis acids, but in the presence of BF_3 -anisole complex, products of different types were obtained.⁶⁾

The reaction of 3-butenol or 3-butenyl chloride with anisole in the presence of aluminium chloride under the similar conditions gave a mixture of 3-(2- and 4-methoxyphenyl)butan-1-ol (72:9, bp 112°C/4 mmHg) or a mixture of 1-chloro-3-(2- and

4-methoxyphenyl)butane (83:17, bp 93-95°C/5 mmHg) in 24 and 55% yield, respectively.

3-(2-Methoxyphenyl)butyl diphenyl phosphate, prepared from 3-(2-methoxyphenyl)-butan-1-ol and diphenyl phosphorochloridate, reacted in the presence of 3- molar equivalents of aluminium chloride to give 4-methylchroman in 45% yield. The result suggested that 3-(2-methoxyphenyl)butyl diphenyl phosphate may be the intermediate of the reaction of 3-butenyl diphenyl phosphate and anisole leading to 4-methylchroman.

Table Reaction of 3-butenyl or 3-methyl-3-butenyl diphenyl phosphate with phenol derivatives in the presence of a Lewis acid

Substituent		Lewis acid	Ratios of II/I/Lewis acid	Product ^a		III yield(%) ^b	b.p. (°C/mmHg)
X	R			R	X		
OH	CH ₃	BF ₃ ·Et ₂ O	1/5/1	CH ₃	H	trace	
OH	CH ₃	SnCl ₄	1/5/1	CH ₃	H	54	57-59/3 ^{1), 2)}
1-OH, 2-CH ₃	CH ₃	BF ₃ ·Et ₂ O	1/5/1	CH ₃	8-CH ₃	14	41-45/3
1-OH, 2-OCH ₃	CH ₃	BF ₃ ·Et ₂ O	1/5/1	CH ₃	8-OCH ₃	17	100-102/3.5
1-OH, 2-OCH ₃	CH ₃	SnCl ₄	1/5/1	CH ₃	8-OCH ₃	25	104-109/3
OCH ₃	CH ₃	SnCl ₄	1/5/1	CH ₃	H	23	76-77/6.5
OCH ₃	CH ₃	AlCl ₃	1/5/1	CH ₃	H	21	55-56/3
OCH ₃	H	AlCl ₃	1/5/3	H	H	20	54-65/4 ³⁾
OH	H	AlCl ₃	1/1/2	H	H	10	54-65/4
1-OH, 2-CH ₃	H	AlCl ₃	1/1/2	H	8-CH ₃	19	67-74/2
1-OH, 3-CH ₃	H	AlCl ₃	1/1/2	H	5-CH ₃ ⁴⁾	11	56-74/2
				H	7-CH ₃		
1-OH, 4-CH ₃	H	AlCl ₃	1/1/2	H	6-CH ₃	12	63-70/3 ⁵⁾

^a In most cases, the products were isolated by preparative g.l.c. and their structures were determined by NMR, IR and elementary analyses.

^b Based on diphenyl phosphate.

Acknowledgment-----The authors are indebted to Professor T. Matsuura of Kyoto University and Lecturer M. Muto of Nagoya Institute of Technology for their helpful comments.

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(Received March 8, 1976)