

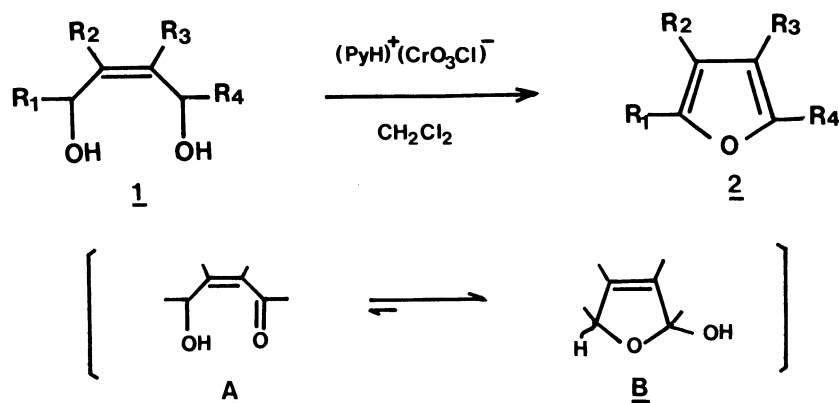
EFFICIENT TRANSFORMATION OF (Z)-2-BUTENE-1,4-DIOLS
TO SUBSTITUTED FURANS WITH PYRIDINIUM CHLOROCHROMATE (PCC)

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(Z)-2-Butene-1,4-diols were efficiently converted to the corresponding substituted furans by one step oxidation-dehydration process with pyridinium chlorochromate (PCC).

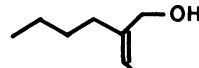
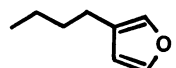
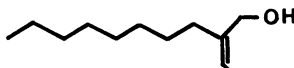
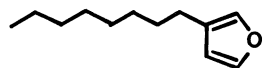
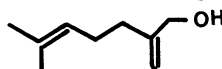
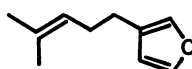
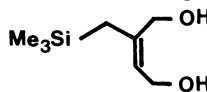
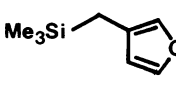
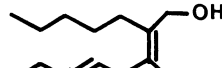
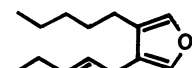
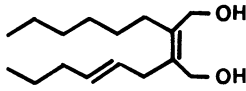
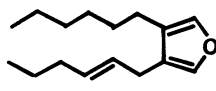
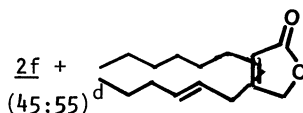
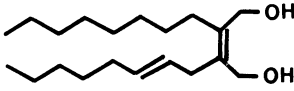
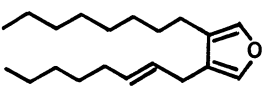
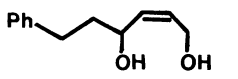
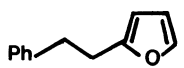
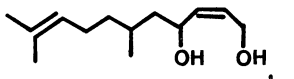
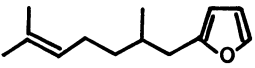
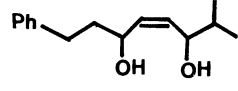
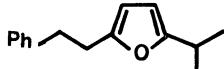
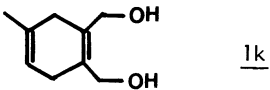
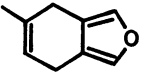
A versatile method for the construction of substituted furan skeletons via (Z)-2-butene-1,4-diols has not been achieved yet.¹ In connection with our studies on the preparation of substituted maleic acid diesters,^{2,3} we are interested in a new route for synthesis of 3- or 3,4-substituted furans via (Z)-2-butene-1,4-diols which are obtained readily from these maleates. We wish to describe here a highly efficient conversion of (Z)-2-butene-1,4-diols to substituted furans with pyridinium chlorochromate (PCC).⁴



Treatment of (Z)-2-butene-1,4-diols 1a-1k with PCC in dichloromethane at room temperature afforded substituted furans 2a-2k in high yields (Table 1).⁵ PCC has sufficiently acidic⁶ to cause the spontaneous dehydration of the intermediary hemiacetal B to furan 2.

Other oxidants were examined for this purpose with 1f (Entry 8-11). Jones' oxidation⁷ gave 2f in a low yield. Collins' oxidation⁸ yielded a mixture of 2f and butenolide, which was formed via rapid allylic oxidation of hemiacetal B. With pyridinium dichromate (PDC)⁹ or active manganese dioxide 1f gave 2f in good to excellent yields. Treatment of 2-trimethylsilylmethyl-(Z)-2-butene-1,4-diol

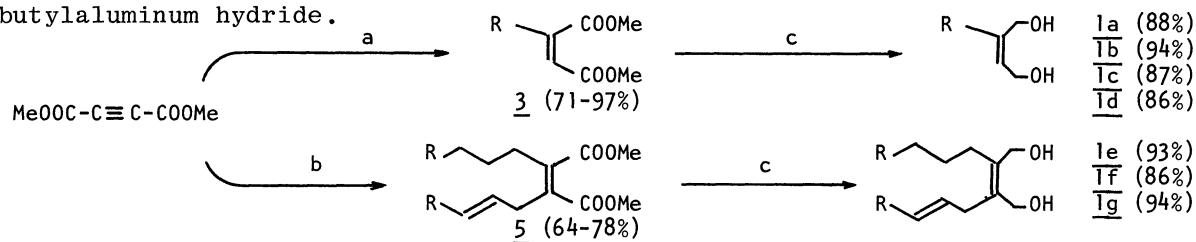
Table 1. Transformation of (Z)-2-Butene-1,4-diols to Substituted Furans

Entry	(Z)-2-Butene-1,4-diol <u>1</u>	Reagent ^a	Substituted Furan <u>2</u>	Yield(%) ^b
1	 <u>1a</u>	PCC	 <u>2a</u>	81
2	 <u>1b</u>	PCC	 <u>2b</u>	84
3	 <u>1c</u>	PCC	 <u>2c</u>	85
4	 <u>1d</u>	PCC ^c	 <u>2d</u>	20
5	„	act. MnO ₂	„	58
6	 <u>1e</u>	PCC	 <u>2e</u>	91
7	 <u>1f</u>	PCC	 <u>2f</u>	91
8	„	PDC	„	65
9	„	act. MnO ₂	„	84
10	„	Jones'	„	6
11	„	Collins'	 ^d	98
12	 <u>1g</u>	PCC	 <u>2g</u>	89
13	 <u>1h</u>	PCC	 <u>2h</u>	35
14	 <u>1i</u>	PCC	 <u>2i</u>	54
15	 <u>1j</u>	PCC	 <u>2j</u>	54
16	 <u>1k</u>	PCC	 <u>2k</u>	73

a. PCC (1.5-1.8 equiv. of 1) and 1 mmol of 1 in 12 ml of CH₂Cl₂, r.t., 30 min. The reaction mixture was extracted with ether. After concentration, the residual oil was purified by silica gel column chromatography to give 2. PDC (2 equiv. of 1), r.t., 1 hr. Active MnO₂ (ca. 50 equiv. of 1) in CH₂Cl₂, r.t., 1 hr. b. Isolated yield. c. Buffered with sodium acetate (PCC/NaOAc=1). d. Determined by ¹H-NMR.

1d with PCC gave the corresponding furan 2d in a low yield, because of lability of allylsilane skeleton of 1d in the acidic medium, whereas the oxidation with active manganese dioxide yielded 2d efficiently (Entry 5).

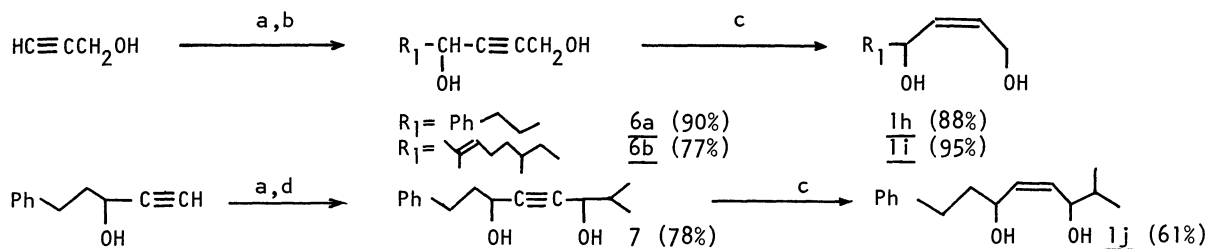
These (Z)-2-butene-1,4-diols were readily prepared by the following methods. 2-Substituted diols 1a-1d were prepared from dimethyl acetylenedicarboxylate (DMAD) via the stereoselective alkylation with organocopper-dimethyl sulfide complexes² followed by reduction with lithium n-butyldiisobutylaluminum hydride.¹⁰ 2,3-Disubstituted diols 1e-1g were prepared by palladium(0) catalyzed cotrimerization of DMAD and 1-olefins³ and following reduction with lithium n-butyldiisobutylaluminum hydride.



a. $R-Cu(Me_2S) \cdot MgX_2$, THF²; b. $Pd(0)$, $RCH_2CH=CH_2$, $CHCl_3$ ³; c. $Li(n-Bu)(i-Bu)_2AlH$, toluene.

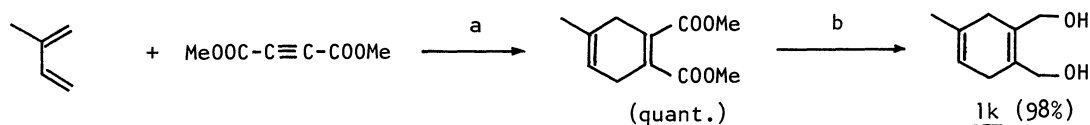
As an application of the present method, perillene¹¹, an ant's alarm pheromone, was synthesized from DMAD in this sequence via the corresponding maleate² and the (Z)-2-butene-1,4-diol 1c, and was obtained in 53% total yield. Thus, we have opened a new route for synthesis of 3- or 3,4-substituted furans from DMAD in three steps.

1- And 1,4-substituted diols 1h-1j were prepared by the alkylation of propargyl alcohols and the subsequent hydrogenation of butyne-1,4-diols 6 and 7.



a. $2 EtMgBr$, Et_2O , r.t.; b. R_1CHO ; c. H_2 , cat. $Pd(0)-BaSO_4$, TMEDA, $CaCO_3$, MeOH, r.t.; d. $(CH_3)_2CHO$.

Cyclohexadiene diol 1k was obtained by Diels-Alder reaction of DMAD and isoprene followed by reduction with lithium n-butyldiisobutylaluminum hydride.¹²



a. benzene, $60^\circ C$, 1 day, in a sealed tube; b. $Li(n-Bu)(i-Bu)_2AlH$, toluene.

References

1. a) Annual Reports in Organic Synthesis, J. McMurry, R.B. Miller, L.S. Hegedus, S.R. Wilson, L.G. Wade, Jr., and M.J. O'Donnel, Part IV, B (1970-1979), Academic Press. Also new useful methods for preparation of substituted furans were reported recently. See follows.
b) K. Inomata, S. Aoyama, and H. Kotake, Bull. Chem. Soc. Jpn., 51, 930 (1978).
c) M. Stahle and M. Schlosser, Angew. Chem., Int. Ed. Engl., 18, 875 (1979).
d) Y. Kojima and N. Kato, Tetrahedron Lett., 4365 (1980).
e) After the submission of this paper, an independent paper on a similar transformation was reported; L.P.J. Burton and J.D. White, J. Am. Chem. Soc., 103, 3226 (1981).
2. H. Nishiyama, M. Sasaki, and K. Itoh, Chem. Lett., 1981, 905.
3. K. Itoh, K. Hirai, M. Sasaki, Y. Nakamura, and H. Nishiyama, Chem. Lett., 865 (1981).
4. E.J. Corey and J.W. Suggs, Tetrahedron Lett., 2467 (1975).
5. For these furans satisfactory spectroscopic data (NMR, IR, mass spectra) were obtained. $^1\text{H-NMR}(\text{CDCl}_3)$ δ ppm, 2a, 6.23(1H), 7.13(1H), 7.30(1H); 2b, 6.20, 7.20, 7.33; 2c, 6.20, 7.13, 7.20; 2d, 6.08, 7.01, 7.21; 2e, 7.07(s, 2H); 2f, 7.07; 2g, 7.07; 2h, 5.94(1H), 6.22(1H), 7.23(1H); 2i, 5.95, 6.23, 7.26; 2j, 5.86(s, 2H); 2k, 7.12(s, 2H) as protons of furan rings.
6. a) E.J. Corey, H.E. Ensley, and J.W. Suggs, J. Org. Chem., 41, 380 (1976).
b) E.J. Corey and D.L. Boger, Tetrahedron Lett., 2461 (1978).
c) W.G. Dauben and D.M. Michno, J. Org. Chem., 42, 682 (1977).
d) G. Piancatelli, A. Screttri, and M.D. Auria, Tetrahedron Lett., 219 (1977).
7. A. Bowers, T.G. Halsall, E.R.H. Jones, and A.J. Lemin, J. Chem. Soc., 2548 (1953); E.J. Eisenbrum, Org. Syn., 45, 28 (1965).
8. J.C. Collins, W.W. Hess, and F.J. Frank, Tetrahedron Lett., 3363 (1968).
9. E.J. Corey and G. Schmidt, Tetrahedron Lett., 399 (1979).
10. G. Kovács, G. Galambos, and Z. Juvancz, Synthesis, 171 (1977); This reagent is superior for 1,2-reduction of α,β -unsaturated esters to lithium aluminum hydride or diisobutylaluminum hydride. With the latter hydrides 3 or 5 gave (Z)-2-butene-1,4-diols 1a-1g (43-63%), but yielded concurrent conjugate reduction products (25-47%).
11. R. Bernardi, C. Cardani, D. Ghirighelli, A. Silva, A. Boggini, and M. Povan, Tetrahedron Lett., 3893 (1967).
12. D. Butina and F. Sondheimer, Synthesis, 543 (1980); The reduction of dimethyl 1-cyclohexene-1,2-dicarboxylate with diisobutylaluminum hydride and subsequent esterification work-up were reported to give the corresponding diol in 20% yield. Furthermore, it was reported that the diol afforded butenolide in 66% yield by oxidation with active manganese dioxide.

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