for 60 min to promote decarboxylation. However, since the bicyclic hydroquinone derivative produced by decarboxylation is not easily purified (ref 13), this gummy residue (260 mg after filtration and solvent removal) was dissolved in ether (50 mL; filtered to clarify) and oxidized with activated MnO_2 (400 mg, 4.6 mmol) by stirring at room temperature for 90 min. The ethereal oxidation mixture was then filtered through a Celite bed and dried over anhydrous sodium sulfate, and the solvent was removed by rotary evaporation to provide crude quinone **5**, which was purified by sublimation (50 °C at 0.05 mmHg). The purified yellow quinone **5** showed mp 65–67 °C (lit.[13] mp 66–67 °C).

Preparation of Diels–Alder Adduct 6. To 72 mg (0.4 mmol) of yellow quinone **1c** in 15 mL of benzene at room temperature was added with stirring 0.07 mL (0.85 mmol) of freshly distilled cyclopentadiene. The initial deep yellow color of the solution faded within 1 min to pale yellow. After stirring for 10 min, the solvent volume was reduced to 1.0 mL by rotary evaporation. In a short time the product (**6**) crystallized as pale-yellow plates (80 mg, 80% yield): mp 121–123 °C, ^1H NMR ($CDCl_3/Me_4Si$) δ OH 7.26 (s, 2 H); olefinic-CH 6.17 (dd, J = 5.9 Hz, J = 3.1 Hz) and 6.12 (dd, J = 5.9 Hz, J = 2.8 Hz); bridgeheads 1- and 4-CH 3.68 (m, 2 H); 4a- and 8a-CH 3.55 (dd, J = 8.0 Hz, J = 4.0 Hz); 9-CH_2 1.67 (dt, J_d = 9.0 Hz, J_t = 1.8 Hz) and 1.55 (dt, J_d = 9.0 Hz, J_t = 1.2 Hz); IR (KBr, cm^{-1}) 3400, 3070, 3020, 2995, 2978, 2951, 1708, 1692, 1593; mass spectrum m/e 234 (M^+, 2), 216 (7), 66 (base).

Acknowledgment. We acknowledge the generous financial support of the National Institutes of Health through New Investigator Research Award (T.J.H., Jr.) No. R23-29844. We appreciate the assistance of Mr. Steve Philson, Department of Chemistry, and Mr. Gerald Bratt, Department of Biochemistry, University of Minnesota, in obtaining high-resolution NMR spectra and performing extensive decoupling experiments.

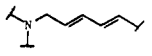
Registry No. **1a**, 5794-62-7; **1b**, 92544-18-8; **1c**, 92544-13-3; **2a**, 92544-15-5; **2b**, 92544-14-4; **3a**, 92544-16-6; **3b**, 92544-17-7; **4**, 92544-19-9; **5**, 6829-72-7; **6**, 92544-20-2; HCl, 7647-01-0; EtSH, 75-08-1; *p*-anisidine, 104-94-9; cyclopentadiene, 542-92-7; gentisic acid, 490-79-9; ceric ammonium sulfate, 7637-03-8.

Communications

Direct Preparation of 5-Amino-1,3-pentadienes through Use of Palladium-Promoted Reactions[1a]

Summary: 5-Amino-1,3-pentadienes are available by condensation of aldehydes and ketones with 1-phosphono-4-(dialkylamino)-2-butenes which in turn are prepared by palladium-catalyzed difunctionalization of 1,3-butadiene.

Sir: The 5-amino-1,3-pentadiene moiety **1** and the corresponding amide system are structural features of several naturally occurring compounds. Some representative



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examples are the kirromycin (mocimycin) antibiotics,[2] the streptogramin antibiotics,[3] the *Asiasarum* and *Fagara amides*,[4] and the macbecin antitumor antibiotics.[5] Various synthetic efforts have been directed toward these diene derivatives previously,[6,7] and herein we report our own

Scheme I

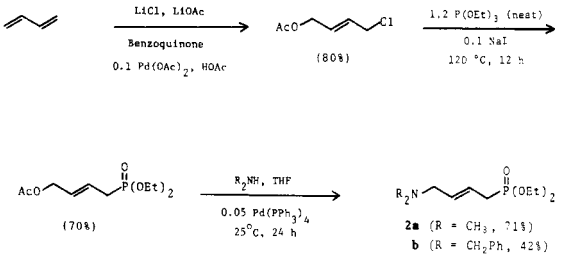
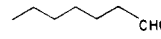
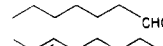
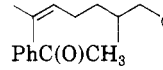


Table I. Condensations of Potassium Derivative of 2

entry	substrate	yield,[a] %	isomer ratio[b]
1	PhCHO	84	2.5:1
2		72	2.5:1
3		79[c]	2.5:1
4		74	2.5:1
5	$PhC(O)CH_3$	66	2.1:1.2:1:1[d]
6		82	3:1
7		42	*e*

[a] Yield of chromatographically purified product obtained using **2a**. [b] Ratio of 2*E*,4*E*:2*E*,4*Z* unless otherwise noted. [c] Obtained using **2b**. [d] 2.1:1.2 2*E*,4*E*:2*E*,4*Z* plus two additional components which appear to be 2*Z* isomers but which were not fully characterized. [e] See ref 16.

(1) (a) This work was presented in part at the 186th National Meeting of the American Chemical Society, Washington, D.C., Aug 1983; Abstract No. ORGN 120. (b) Current address of this author: Department of Chemistry, University of Notre Dame, Notre Dame, IN 46556.

(2) (a) Parmeggiani, A.; Sander, G. In "Topics in Antibiotic Chemistry"; Sammes, P. G., Ed.; Wiley: New York, 1980; Vol. 5, Part C, pp 159–221. (b) Zimmerman, S. B.; Chalmers, J. H. U.S. Pat. 4 071 631, 1978; *Chem. Abstr.* **1978**, *88*, 150593b. (c) Maehr, J.; Leach, M.; Williams, T. H.; Blount, J. F. *Can. J. Chem.* **1980**, *58*, 501–526. (d) Zeeck, A.; Hoppe, H.-U.; Hummel, I. *Tetrahedron Lett.* **1981**, *22*, 2357–2360. (e) Gullo, V. P.; Zimmerman, S. B.; Dewey, R. S.; Hensens, O.; Cassidy, P. J.; Oiwa, R.; Omura, S. *J. Antibiot.* **1982**, *35*, 1705–1707.

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(4) (a) Yasuda, I.; Takeya, K.; Itokawa, H. *Chem. Pharm. Bull.* **1981**, *29*, 564–566. (b) Kubo, I.; Matsumoto, T.; Klocke, J. A.; Kamikawa, T. *Experentia* **1984**, *40*, 340–341.

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(6) For some methods for the synthesis of dienamides corresponding to **1**, see: (a) Sharma, S. D.; Aggarwal, R. C.; Soni, B. R.; Sharma, M. L. *Ind. J. Chem.* **1979**, *18B*, 81–82. (b) Nakai, T.; Setoi, H.; Kageyama, Y. *Tetrahedron Lett.* **1981**, *22*, 4097–4100. (c) Banerji, A.; Pal, S. C. *Phytochem.* **1983**, *22*, 1028–1030. (d) Tsuboi, S.; Nooda, Y.; Takeda, A. *J. Org. Chem.* **1984**, *49*, 1204–1208.

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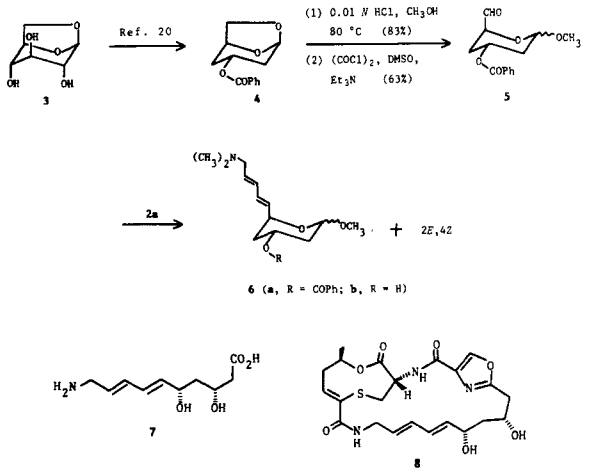
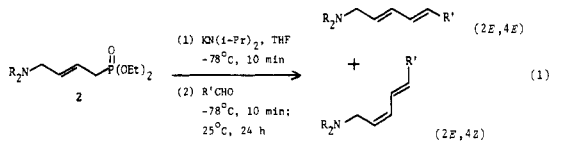
Scheme II



preliminary results in developing a very direct route to these compounds.

We initially explored a multistep procedure employing the condensation of γ-phosphorylcrotonates with aldehydes,[6a,c,8,9] but the use of 1-amino-4-phosphono-2-butenes **2** as reagents for the one-step conversion of carbonyl compounds into the desired amines appeared to be a much more attractive possibility.[10] Palladium-catalyzed difunctionalization of 1,3-dienes[11] is conveniently applicable to the preparation of **2** through use of the chloroacetoxylation reaction,[11d] an Arbuzov reaction,[12] and palladium-catalyzed amination (Scheme I).[13,14]

For condensation[10] with carbonyl compounds (eq 1), we



have observed that the potassium derivative of **2** obtained by using potassium diisopropylamide[15] is generally superior to the lithium derivative. Our results (Table I) indicate that the reaction is apparently general for both aldehydes and ketones, either with or without enolizable protons. A significant yield of desired product is also obtained in the case of the sterically hindered 2,6-dimethylcyclohexanone (Table I, entry 7).[16] With respect to stereochemical behavior, mixtures of 2*E*,4*E* and 2*E*,4*Z* products are usually obtained in 2.5–3:1 ratios.[17,18]

For a further application (Scheme II), optically active levoglucosan (**3**)[19] is converted into the dideoxy derivative **4**[20] followed by methanolysis[21] and oxidation[22] to produce aldehyde **5**.[23] Reaction with **2** gives **6a** and **6b** (1:4) as a 3:1 *E,E*:*E,Z* mixture (combined yield 68%).[23] Product **6** is a protected form of **7** with the same absolute configuration as a key portion of griseoviridin **8** and other streptogramin antibiotics.[3,7]

Improvements in this methodology and applications in natural products synthesis are being pursued in our laboratories.

Acknowledgment. We are very grateful for the most valuable advice and assistance provided by Dr. J.-E. Nyström of the Royal Institute of Technology and for preliminary experimental studies performed by Mr. Charles Meyer at Stony Brook. We are also pleased to acknowledge financial support provided by the Natural Science Research Council (Sweden), the National Science Foundation of the U.S.A. (Grant No. CHE 8120466), the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant 14337-ACl-C), and the American–Scandinavian Foundation, the latter having provided a fellowship to P.H. for a research leave in Stockholm. We thank Johnson Matthey Inc. for generously providing palladium salts. The Nicolet NT-300 NMR spectrometer employed in this work was purchased with funds provided in part by the NSF Instrumentation

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(9) Nicolaou, K. C.; Papahatjis, D. P.; Claremon, D. A.; Dolle, R. E. *J. Am. Chem. Soc.* **1981**, *103*, 6967–6969.

(10) For a review of the use of phosphonates in olefination reactions in general, see: Wadsworth, W. S. *Org. React. (N.Y.)* **1977**, *25*, 73–253.

(11) (a) Brown, R. G.; Davidson, J. M. *J. Chem. Soc. A* **1971**, 1321–1327. (b) Åkermark, B.; Bäckvall, J.-E.; Löwenborg, A.; Zetterberg, K. *J. Organomet. Chem.* **1979**, *166*, C33–C36. (c) Åkermark, B.; Ljungqvist, A.; Panunzio, M. *Tetrahedron Lett.* **1981**, *22*, 1055–1058. (d) Bäckvall, J.-E.; Nordberg, R. E.; Nyström, J.-E. *Ibid.* **1982**, *23*, 1617–1620. (e) Bäckvall, J.-E. *Pure Appl. Chem.* **1983**, *55*, 1669–1676. (f) Bäckvall, J.-E. *Acc. Chem. Res.* **1983**, *16*, 335–342.

(12) Sodium iodide (0.1 equiv) was required to effect an in situ Finkelstein reaction. The chloride itself was unreactive toward triethyl phosphite at 120 °C.

(13) (a) Trost, B. M. *Tetrahedron* **1977**, *33*, 2615–2649. (b) Tsuji, J. *Top. Curr. Chem.* **1980**, *91*, 29–74. (c) Trost, B. M.; Genet, J. P. *J. Am. Chem. Soc.* **1976**, *98*, 8516–8517. (d) Trost, B. M.; Keinan, E. *J. Org. Chem.* **1979**, *44*, 3451–3457. (e) Åkermark, B.; Åkermark, G.; Hegedus, L. S.; Zetterberg, K. *J. Am. Chem. Soc.* **1981**, *103*, 3037–3040. (f) Yamamoto, T.; Saito, O.; Yamamoto, A. *Ibid.* **1981**, *103*, 5600–5602. (g) Godleski, S. A.; Meinhart, J. D.; Miller, D. J.; Van Wallendael, S. *Tetrahedron Lett.* **1981**, *22*, 2247–2250.

(14) In addition to the secondary amines used in the final step of Scheme I, we have also succeeded in employing benzylamine.

(15) Gawley, R. E.; Temine, E. J.; Aube, J. *Tetrahedron Lett.* **1980**, *21*, 3115–3118. Under these conditions, the use of hexamethylphosphoric triamide promotes a much greater rate of reaction, but the overall yields remain approximately the same as reported in Table I. If the solution of metalated **2** is distinctly red or orange rather than light yellow, inferior yields of condensation products are generally obtained.

(16) The assignment of structures to all of the isomeric products of this reaction is difficult due not only to the usual question of diene configuration but also due to the presence of *cis*- and *trans*-dimethyl substitution patterns about the six-membered ring. Because of overlap of signals in the vinyl region of the NMR spectra, we are not able to assign the ratio of diene isomers accurately, but our data are consistent with a 1:1 mixture of the *cis*- and *trans*-dimethyl isomers. See: (a) Johnson, F.; Starkovsky, N. A.; Gurowitz, W. D. *J. Am. Chem. Soc.* **1965**, *87*, 3492–3500. (b) Geneste, P.; Durand, R.; Kamenka, J.-M.; Beierbeck, H.; Martino, R.; Saunders, J. K. *Can. J. Chem.* **1978**, *56*, 1940–1946. (c) Fraser, R. R.; Dhawan, K. L.; Taymaz, K. *Org. Magn. Reson.* **1978**, *11*, 269–274.

(17) All diene configurations were assigned on the basis of 300-MHz ^{1}H NMR spectra which are in agreement with data reported for closely related compounds: Samain, D.; Descoins, C.; Langlois, Y. *Nouv. J. Chim.* **1978**, *2*, 249–254.

(18) To be noted is that the double bond that is formed in the condensation is of the *E* configuration, at least in the cases of aldehyde substrates. The configurational isomers seen for the other double bond imply partial isomerization of **2** under the reactions conditions. Before reaction, **2** appears to be a ca. 9:1 mixture of *E* and *Z* isomers.

(19) (a) Ward, R. B. *Methods Carbohydr. Chem.* **1963**, *2*, 394–396. (b) Coleman, G. H. *Ibid.* **1963**, *2*, 397–399. (c) Private correspondence with Professor B. Fraser-Reid of Duke University.

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(21) Cerny, M.; Stanek, J. *Adv. Carbohydr. Chem. Biochem.* **1977**, *34*, 23–177.

(22) Mancuso, A. J.; Huang, S.-L.; Swern, D. *J. Org. Chem.* **1978**, *43*, 2480–2482.

(23) Each of these compounds exists as a mixture of α- and β-anomers according to NMR data. See: Jurczak, J.; Chmielewski, M.; Zamojski, A. *Polish J. Chem.* **1978**, *52*, 743–749.

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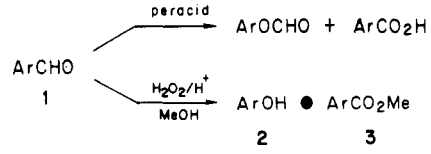
Acid-Catalyzed Oxidation of Benzaldehydes to Phenols by Hydrogen Peroxide

Summary: A wide variety of benzaldehydes were oxidized to phenols by hydrogen peroxide in acidic methanol.

Sir: The oxidation of benzaldehydes to phenols is one of the important synthons in organic synthesis and can be attained by means of Dakin reaction or Baeyer–Villiger reaction by peracids.[1,2] Dakin reaction is, in general, limited to use for the oxidation of hydroxylated benzaldehydes such as salicylaldehydes and *p*-hydroxybenzaldehydes.[2] On the other hand, Baeyer–Villiger reaction of benzaldehydes by peracids is widely applicable for the synthesis of aryl formates and/or benzoic acids. This oxidation is, however, unfavorable for substrates possessing functional groups labile to peracids.

We report here that these defects are overcome by acid-catalyzed oxidation of benzalhydes with hydrogen peroxide in methanol. The characteristic features of the present oxidation are as follows: (i) the reaction is achieved by the use of 30–35% aqueous hydrogen peroxide which is easy to handle, (ii) the oxidation products are phenols and/or methyl benzoates, while aryl formates and/or benzoic acids are the products in the Baeyer–Villiger oxidation by peracids, (iii) olefinic substituents in benzaldehydes are stable under the present reaction conditions, (iv) the reaction appears to proceed through peroxy hemiacetals.

When a solution of 2-methoxybenzaldehyde (**1a**) (5.0 g, 36.7 mmol) and 31% aqueous H_2O_2 (5.3 g, 48 mmol) in methanol (50 mL) was stirred with sulfuric acid (0.5 mL) at room temperature for 24 h, 2-methoxyphenol (**2a**) was produced in a 94% yield. Similarly, a wide variety of other



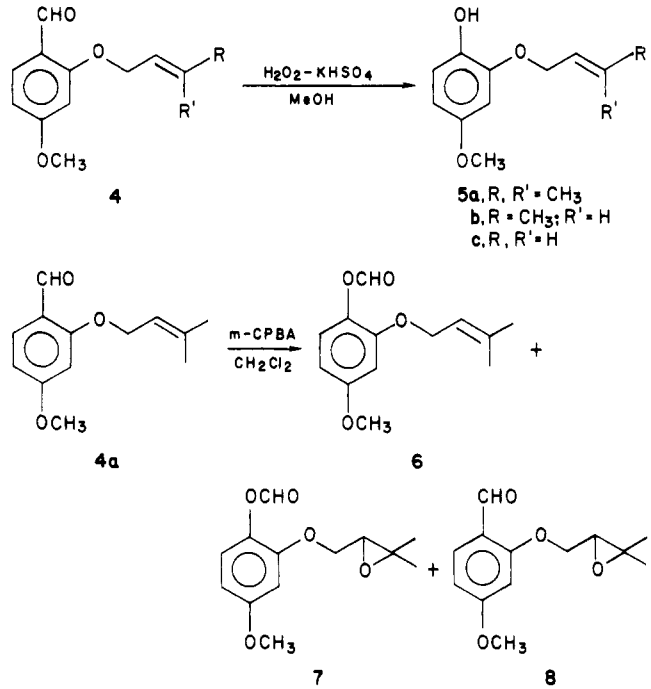
benzaldehydes **1** were oxidized to the corresponding phenols **2** and/or methyl benzoates **3** as cited in Table I. The results showed that, in most cases, the present system gave phenols **2** more selectively than the peracid oxidation, though the migratory aptitude of aryl groups compared with the hydrogen of the aldehyde function were similar to the conventional Baeyer–Villiger oxidation.[3–6]

Table I. Acid-Catalyzed Oxidation of Benzaldehydes by Hydrogen Peroxide[a]

run	benzaldehyde 1	reactn time, h	yield,[c,d] % phenol 2	yield,[c,d] % ester 3
a	2-methoxy	24	94 (60)[4]	
b	3-methoxy	68	(31)[4]	68
c	4-methoxy	24	90 (92)[4]	
d	2,3-dimethoxy	63	30	14
e	2,4-dimethoxy	14	90	
f	3,4-dimethoxy	5	60 (83)[4]	
g	2,3,4-trimethoxy	1	97 (83)[4]	
h	2,4,5-trimethoxy	4	89 (79)[4]	
i	2,4,6-trimethoxy	2	89 (63)[5]	
j	3,4-methylenedioxy	24	67 (58)[6]	8
k	4-methyl	24[b]	28	51
l	4-chloro	24[b]		87
m	4-nitro	12[b]		80

[a] Unless otherwise stated, benzaldehyde **1** (5 mmol) and 31% H_2O_2 (6.4 mmol) were stirred in the presence of H_2SO_4 (0.1 mL) in methanol (10 mL) under an argon atmosphere at room temperature. [b] The reaction mixture was heated at refluxing temperature. [c] All the products were isolated by chromatography (SiO_2). [d] Figures in parentheses are the yields of phenols by peracid oxidation of the corresponding benzaldehydes followed by hydrolysis.

The superiority of the present system was strikingly shown in the oxidation of 4-methoxy-2-(3-methyl-2-buten-1-yloxy)benzaldehyde (**4a**). Treatment of **4a** (0.75 g) with H_2O_2 (31%, 470 mg) in acidic methanol [$KHSO_4$ (70 mg), 7 mL] at room temperature for 4 h gave the corresponding phenol **5a** in a 80% yield. By contrast, the oxidation of **4a** with *m*-chloroperbenzoic acid gave a mixture of a formate **6** (18% yield) and epoxides **7** (30% yield) and **8** (40% yield). The other (allyloxy)benzaldehydes **4b** and **4c** were also selectively converted into phenols **5b** (97% yield) and **5c** (83% yield), respectively, by the H_2O_2/MeOH/H^+ oxidation.



The present oxidation is a type of Baeyer–Villiger oxidation. To account for the formation of phenols **2** and/or

(1) For a review, see: Hassall, C. H. "Organic Reactions"; Wiley: New York, 1967; Vol. 9, pp 73–106.
(2) For a review, see: Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. 1, p 467. See also ref 1.
(3) For a review, see: Trahanovsky, W. S. "Oxidation in Organic Chemistry"; Academic Press: New York, 1978; Part C, p 254.
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(5) Hüe, R.; Jubier, A.; Andrieux, J.; Resplandy, A. *Bull. Soc. Chim. Fr.* **1970**, 3617.
(6) Beroza, M. *J. Agric. Food. Chem.* **1956**, *4*, 50.

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