Acknowledgment. We thank Dr. W. A. Gilbert for his graphic analysis of **1a** and the National Science Foundation and Hoffmann-La Roche (unrestricted grant awarded to S. Masamune) for financial support. S. Murakami is on leave from Yoshitomi Pharmaceutical Industries, Ltd., Japan. High-resolution mass spectra were provided by the facility, supported by the National Institutes of Health (Grant RR 00317; principal investigator, Professor K. Biemann), from the Biotechnology Resources Branch, Division of Research Resources.

Supplementary Material Available: Listings of final atomic parameters, final anisotropic thermal parameters, bond lengths, and bond angles (7 pages). Ordering information is given on any current masthead page.

(19) **Note Added in Proof:** After the submission of this paper a report on the synthesis of a disilene derivative appeared: West, R.; Fink, M. J.; Michl, J. *Science* **1981**, *214*, 1343. Also see: *Chem. Eng. News* **1981**, *Dec. 21*, 8.

Total Synthesis of Racemic Chorismic Acid

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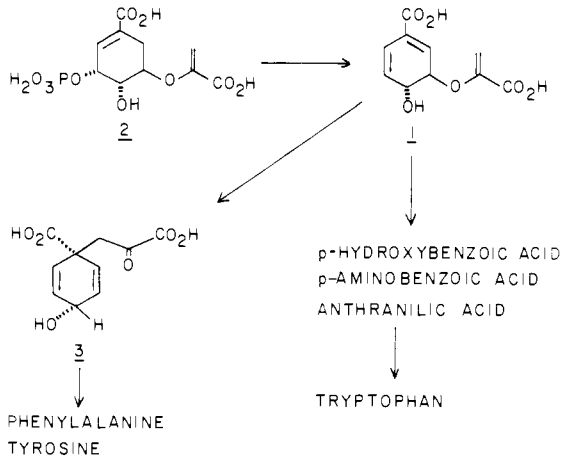
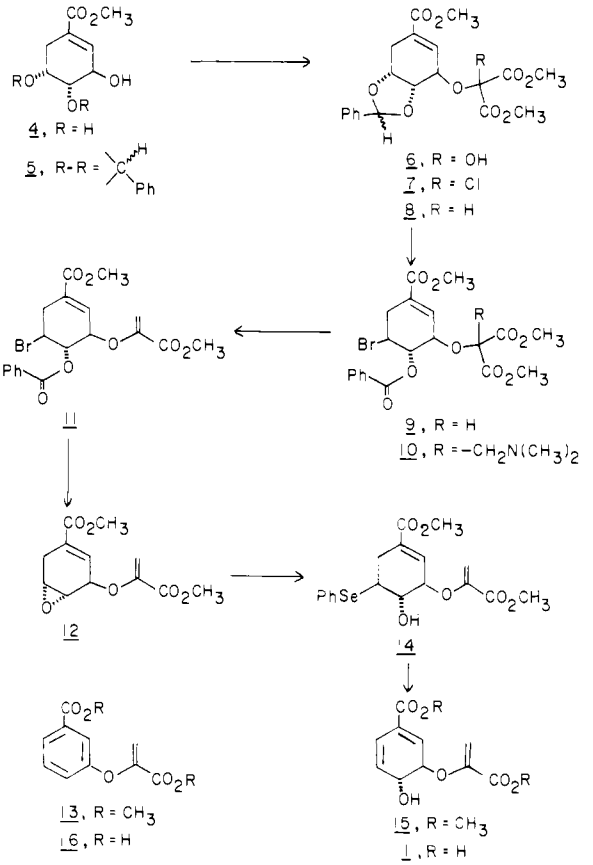
Chorismic acid (**1**) occupies the unique position of being the last common intermediate in the biosynthesis of aromatic substances through the shikimate pathway in bacteria, fungi, and higher plants.[1] Despite intensive efforts by numerous research groups, unambiguous confirmation of a branch-point intermediate beyond 5-enolpyruvylshikimic acid 3-phosphate (**2**) and establishment of the structure of this intermediate remained a mystery until Gibson and co-workers developed a mutant of *A. aerogenes* from which **1** was isolated (initially as the barium salt and later as the stable dicarboxylic acid),[2-4] and the structure and absolute stereochemistry were established.[5] Gibson and collaborators, in particular, and others capitalized on this discovery to elucidate detailed information on the biosynthetic pathway from **1** to the aromatic substances indicated in Scheme I and to numerous other aromatic derivatives.[1] The chorismic pathway remains an area of intensive study, and the rearrangement of **1** to prephenic acid (**3**), presumably a Claisen rearrangement,[6-9] is most unusual as an enzyme-catalyzed transformation.

The important biosynthetic role and the unique structure of **1** have attracted considerable attention. Disodium prephenate (free-acid unstable) recently has yielded to total synthesis;[10,11] but, although known for nearly 2 decades, **1** previously has not yielded to total synthesis.[12] Described below is our total synthesis of racemic **1**.

Scheme I



Scheme II



Starting material for the synthesis (Scheme II) was methyl 4-*epi*-shikimate (**4**).[13] Protection of the C_4 and C_5 hydroxyl groups was effected by reaction of **4** with benzaldehyde (catalyzed by TsOH; toluene, reflux) to give a 3:2 mixture of benzylidine acetals, **5**,[16] in 72% yield. Functionalization of the C_3 hydroxyl group of

(1) For detailed reviews, see: (a) Weiss, U.; Edwards, J. M. "The Biosynthesis of Aromatic Compounds"; Wiley: New York, 1980. (b) Haslam, E. "The Shikimate Pathway"; Halstead Press, Wiley: New York, 1974.
(2) Gibson, M. I.; Gibson, F. *Biochem. Biophys. Acta* **1962**, *65*, 160-163.
(3) Gibson, F.; Jackman, L. M. *Nature* **1963**, *198*, 388-389.
(4) Gibson, F. *Methods Enzymol.* **1970**, *17A*, 362-364 and references cited therein.
(5) Edwards, J. M.; Jackman, L. M. *Aust. J. Chem.* **1965**, *18*, 1227-1239.
(6) Andrews, P. R.; Haddon, R. C. *Aust. J. Chem.* **1979**, *32*, 1921-1929.
(7) Görisch, H. *Biochemistry* **1978**, *18*, 3700-3705.
(8) Andrews, P. R.; Cain, E. N.; Rizzardo, E.; Smith, G. D. *Biochemistry* **1977**, *16*, 4848-4852.
(9) Andrews, P. R.; Smith, G. D.; Young, I. G. *Biochemistry* **1973**, *12*, 3492-3498.
(10) Danishefsky, S.; Hirama, M. *J. Am. Chem. Soc.* **1977**, *99*, 7740-7741; Danishefsky, S.; Hirama, M.; Fritsch, N. Clardy, J. *J. Am. Chem. Soc.* **1979**, *101*, 7013-7018.
(11) Gramlich, W.; Plieninger, H. *Tetrahedron Lett.* **1978**, 3619-3622. *Chem. Ber.* **1979**, *112*, 1550-1570, 1571-1584.

(12) A synthesis of norchorismic acid, where the C_3 substituent is $-OCH_2CO_2H$ rather than the enolpyruvyl moiety, has been reported: Ikota, N.; Ganem, B. *J. Chem. Soc., Chem. Commun.* **1978**, ,869-870.
(13) Although preparation of **4** and 4-*epi*shikimic acid is described in the literature,[14,15] we found an alternate procedure to **4** from methyl 2,5-dihydrobenzoate to be more practical. Epoxidation (CH_3CO_3H) and treatment with base afforded methyl 3-hydroxy-2,3-dihydrobenzoate, which underwent syn epoxidation (*m*-CPBA) at C_4-C_5. Solvolysis of the epoxide with acetic acid and treatment with CH_3O^-/CH_3OH gave pure **4** in ~20% overall yield after recrystallization. Details will be presented in a full paper.
(14) Grewe, R.; Kersten, S. *Chem. Ber.* **1967**, *100*, 2546-2553.
(15) Snyder, C. D.; Rapoport, H. *J. Am. Chem. Soc.* **1973**, *95*, 7821-7828.

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5 to afford malonate derivative 8 (46% from 5) was accomplished by reaction with dimethyl oxomalonate[17] to obtain 6, conversion to chloride 7 ($SOCl_2$, pyridine, THF), and reduction (Zn, HOAc).[18] Cleavage of the acetal functionality of 8 (NBS, C_6H_6) afforded crystalline 9 (64%).[19]

Construction of the enolpyruvate ester moiety from malonate derivative 9 was achieved by formation of Mannich base 10 [$CH_2{=}N^+(CH_3)_2I^-$, $(C_2H_5)_3N$, CH_2Cl_2], quaternization of the amino group (CH_3I, CH_2Cl_2), and thermolysis at 80-85 °C in dimethyl sulfoxide to obtain 11[20] (47% from 9). Reaction of 11 with CH_3O^- in CH_3OH gave 12 and a small amount of 13 (~15%) from which pure, crystalline epoxide 12[21] (46%) was obtained by crystallization from CH_3OH. Epoxide 12 underwent regiospecific ring opening with $PhSe^-$ (Ph_2Se_2, $NaBH_4$, CH_3OH) to give 14.[22] Treatment of 14 with 30% H_2O_2 in CH_2Cl_2:THF at 0 °C afforded the selenoxide derivative. After addition of 3 equiv of $NaHCO_3$, the mixture was kept at room temperature for 1.5 h, during which time selenoxide elimination occurred to give dimethyl chorismate (15)[23,24] in 28% yield from 12.

Hydrolysis of 15 (2.2 equiv of NaOH in THF-H_2O, 3.5 h, 0 °C) followed by treatment with Amberlite IR-120 resin and removal of water afforded a 3:2 mixture of 1 and 16 from which pure, racemic 1 was obtained by successive recrystallization from ethyl acetate/hexane. The IR, UV, NMR, and mass spectral data of synthetic 1 (mp 139.5-141 °C dec) were identical with the spectral data of 1 obtained from culture growth of *A. aerogenes* (62-1).[5,26]

Acknowledgment. We are grateful to the National Institutes of Health, Grant GM 19103, for financial support.

(16) Satisfactory spectral data have been obtained for all new substances described. Satisfactory analytical data (combustion or high-resolution mass spectrum) have been obtained for 1, 4, 5, 7, 9, 11, 12, and 15. High-resolution mass spectra were provided by the facility supported by National Institutes of Health Grant RR00317 (principal investigator Professor K. Biemann) from the Biotechnology Resources Branch, Division of Research Resources.

(17) The most convenient preparation of dimethyl oxomalonate is by modification of Salomon's procedure for the diethyl ester: Pardo, S. N.; Salomon, R. G. *J. Org. Chem.* **1981**, *46*, 2598-2599.

(18) The sequence 5 → 8 is based on literature procedures developed to effect similar substitution on the nitrogen atom of β-lactams: (a) Schmitt, S. M.; Johnston, D. B. R.; Christensen, B. G. *J. Org. Chem.* **1980**, *45*, 1135-1142, 1142-1148. (b) Scartazzini, R.; Peter, H.; Bickel, H.; Heusler, K.; Woodward, R. B. *Helv. Chim. Acta* **1972**, *55*, 408-417.

(19) Cleavage of the acetal group of 8 is not regiospecific. The 4-bromo-5-benzoyloxy derivative is obtained also (24%), and the two isomers are separated by chromatography on silica gel. Although we used only isomer 9 for further transformations, in principle it should be possible to convert the second isomer to 12 by procedures similar to those used to convert 9 to 12.

(20) 11: IR (CH_2Cl_2) 1721, 1619 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 8.03 (dd, 2 H, J = 8.5, 1.5 Hz, *o*-ArH), 7.59 (t, 1 H, J = 7 Hz, *p*-ArH), 7.46 (dt, 2 H, J = 7.7, 2 Hz, *m*-ArH), 6.94 (dd, 1 H, J = 2.7, 1.7 Hz, H_2), 5.73 (dd, 1 H, J = 10.7, 7.3 Hz, H_4), 5.50 (d, 1 H, J = 2.6 Hz, *trans*-OC=CH), 4.93 (m, 1 H, H_3), 4.88 (d, 1 H, J = 2.6 Hz, *cis*-OC=CH), 4.34 (dt, 1 H, J = 10.3, 5.9 Hz, H_5), 3.80 (s, 3 H, OCH_3), 3.69 (s, 3 H, OCH_3), 3.27 (dd, 1 H, J = 18.2, 5.7 Hz, H_6), 2.99 (m, 1 H, H_6).

(21) 12: mp 119-120 °C; IR (CH_2Cl_2) 1720, 1621 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 6.83 (m, 1 H, H_2), 5.59 (d, 1 H, J = 3.3 Hz, *trans*-OC=CH), 4.94 (m, 1 H, H_3), 4.93 (d, 1 H, J = 3.3 Hz, *cis*-OC=CH), 3.82 (s, 3 H, OCH_3), 3.76 (s, 3 H, OCH_3), 3.48 (m, 1 H, H_4 or H_5), 3.40 (m, 1 H, H_4 or H_5), 2.94 (br d, 1 H, J = 19.8 Hz, H_6), 2.76 (br d, 1 H, J = 19.8 Hz, H_6).

(22) 14: ^1H NMR ($CDCl_3$, 250 MHz) δ 7.6-7.2 (m, 5 H, Ar-H), 6.71 (br s, 1 H, H_2), 5.58 (d, 1 H, J = 2.9 Hz, *trans*-OC=CH), 4.89 (d, 1 H, J = 2.9 Hz, *cis*-OC=CH), 4.67 (m, 1 H, H_3), 3.81 (s, 3 H, OCH_3 and m, 1 H, H_4), 3.71 (s, 3 H, OCH_3), 3.42 (s, 1 H, OH), 3.30 (dt, 1 H, J = 11.4, 5.4 Hz, H_5), 2.95 (dd, 1 H, J = 18.1, 5.3 Hz, H_6), 2.46 (m, 1 H, H_6).

(23) 15: mp 94-96 °C; IR (CH_2Cl_2) 1730, 1627 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 6.91 (br s, 1 H, H_2), 6.35 (br d, 1 H, J = 10.3 Hz, H_5 or H_6), 6.05 (dd, 1 H, J = 10.3, 2.0 Hz, H_5 or H_6), 5.56 (d, 1 H, J = 2.9 Hz, *trans*-OC=CH), 4.90 (d, 1 H, J = 13.2 Hz, H_3 or H_4), 4.86 (d, 1 H, J = 13.2 Hz, H_3 or H_4), 4.80 (d, 1 H, J = 2.9 Hz, *cis*-OC=CH), 3.83 (s, 3 H, OCH_3), 3.79 (s, 3 H, OCH_3), 3.15 (br s, 1 H, OH); ^{13}C NMR ($CDCl_3$) 164.7 (s), 163.6 (s), 149.4 (s), 133.7 (d), 132.0 (d), 129.4 (s), 121.7 (d), 98.7 (t), 81.6 (d), 70.9 (d), 52.6 (q), 52.1 (q).

(24) The IR and ^1H NMR spectral data were in agreement with those reported for 15 prepared from reaction of CH_2N_2 with 1 isolated from culture growth of *A. aerogenes*.[25]

(25) Ife, R. J.; Ball, L. F.; Lowe, P.; Haslam, E. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1776-1783.

(26) We thank Professor F. Gibson for providing a sample of *A. aerogenes* (62-1).

Hexamethylenetetratellurafulvalene

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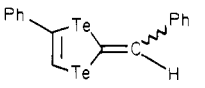
One of the most formidable challenges to the designer of organic metals over the past eight years has been the preparation of tellurium analogues of tetrathiafulvalene (TTF) and its alkylated derivatives.[1] Engler[2] and Cowan[3] have shown that dramatic changes in physical properties can be gained in going from the thiafulvalene to selenafulvalene TCNQ salts. Of these, hexamethylenetetraselenafulvalene was the most interesting because its TCNQ salt behaved like a semimetal,[4] and contrary to all other members of its class it did not become an insulator at low temperature. More recently, Bechgaard[5] showed that tetramethyltetraselenafulvalene (TMTSF) could be converted to a family of salts [$(TMTSF)_2$ X; X = univalent anion], one of which [$(TMTSF)_2ClO_4$] was found to be a superconductor at 1.3 K. Would the tellurium analogue be a superconductor at higher temperature?

In this communication we report on the first directed synthesis of a tetratellurafulvalene. All previous reports on organotellurium chemistry dealt with methodology for carbon-tellurium bond-forming reactions.

Work on the synthesis of a tellurafulvalene was pursued very seriously only after the Russian claim[7] that a 1,3-ditellurole (1)



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could be isolated without difficulty and that it was stable.[6] Prior to this finding, it was assumed that such a molecule (and consequently the tellurafulvalenes) would be very unstable because tellurium was thought to be too large (covalent radius 1.37 Å) to be incorporated into a five-membered heterocycle with the two tellurium heteroatoms in a 1,3 relationship.

The heterocycle 1 (cis isomer) was prepared in reasonable yield along with a number of small-ring telluroheterocycles[7] via phenyltelluroacetylide ($PhC{\equiv}CTe^-Na^+$) in a modified version of the original claim. One of the most versatile synthetic reactions for the preparation of tellurium heterocycles is the addition of telluride to an acetylene linkage,[8] and synthetic schemes for the preparation of 1,3 ditelluroles based on this reaction were reported[9] and are being explored.

Scheme I (with the following conditions: (i) 2*t*-BuLi, THF, -80 °C; (ii) Te, -15 °C; (iii) $Cl_2C{=}CCl_2$, -80 to 25 °C) depicts our approach to the title compound, 7. From the outset we were pessimistic about the coupling of two ditellurole moieties, the most effective method employed for the preparation of thia- and sel-

(1) "The Physics and Chemistry of Low Dimensional Solids"; L. Alcacer, Ed.; D. Reidel Publishing Co.: Dordrecht, Holland, 1980.

(2) Engler, E. M.; Patel, V. V.; Andersen, J. R.; Tomkiewicz, Y.; Craven, R. A.; Scott, B.; Etemad, W. *Ann. N.Y. Acad. Sci.* **1978**, *313*, 343 and references therein.

(3) Bloch, A. N.; Carruthers, T. F.; Poehler, T. O.; Cowan, D. O. In "Chemistry and Physics of One Dimensional Metals"; H. J. Keller, Ed.; Plenum: New York, 1977; p 47. Cowan, D. O.; Shu, P.; Hu, C.; Krug, W.; Carruthers, T. F.; Poehler, T. O.; Bloch, A. N. *Ibid.*, p 25.

(4) Reference 3. Jerome, D.; Weger, M. In ref 3, p 341.

(5) Bechgaard, K.; Carneiro, K.; Rassmussen, F. B.; Rinsdorf, G.; Jacobsen, C. S.; Pedersen, H. J.; Scott, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 2440 and references therein.

(6) Petrov, M. L.; Iaihev, V. Z.; Petrov, A. A. *Russ. J. Org. Chem.* (*Engl. Transl.*) **1979**, *15*, 2346.

(7) The Russian claim was premature; see: Lakshmikantham, M. V.; Cava, M. P.; Albeck, M.; Engman, L.; Wudl, F.; Aharon-Shalom, E. *J. Chem. Soc., Chem. Commun.* **1981**, 828. Bender, S. L.; Haley, N. F.; Luss, H. R. *Tetrahedron Lett.* **1981**, *22*, 1495.

(8) Lehner, W.; Praefcke, K. *Chem. Ber.* **1978**, *111*, 3745.

(9) Sukhai, R. S.; Verboow, W.; Meijer, J.; Schoufs, M. J. M.; Brandsma, I. *Recl. Trav. Chim. Pays-Bas* **1981**, *100*, 10.

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