crystallography and is shown in Figure 1.[18] The bond lengths and angles are summarized in Table I.

The diene **2** also undergoes facile Diels–Alder reaction and reacts with bromine to form a dibromide with internal bridging to give another bicyclo[2.2.0]hexane derivative.[19] The details of these and other reactions will be presented subsequently.

Acknowledgment. This investigation was supported by NSF Grant CHE-78-27880 and, in part, by NSF Grant CHE-79-16210 (high-field NMR spectrometer).

Supplementary Material Available: Positional parameters, bond distances, and bond angles with their estimated standard deviations for **7** (2 pages). Ordering information is given on any current masthead page.

(18) Crystal data: space group *Pbca*; $a = 9.580$ (2), $b = 9.258$ (2), $c = 11.012$ (2) Å, $Z = 4$. Diffraction data were collected on an Enraf–Nonius CAD-4 diffractometer: 932 reflections ($F^2 \geq 3.05\ F^2$) were used in the structure solution and refinement. The structure was solved by direct methods using the program MULTAN and 132 reflections having $E_{min} \geq 1.45$. All programs were those of the Enraf–Nonius SDP program library. Final values of the residuals were $R = 0.043$ and $R_w = 0.045$.

(19) The ^{13}C NMR spectrum indicates the absence of a C–C double bond in the product as well as a symmetry corresponding to that of **2**. The analysis indicates two bromines. In principle, bridging could occur in two ways, but models indicate that only bridging to form the bicyclo[2.2.0]hexane ring is possible.

Total Synthesis of Pretyrosine (Arogenate)

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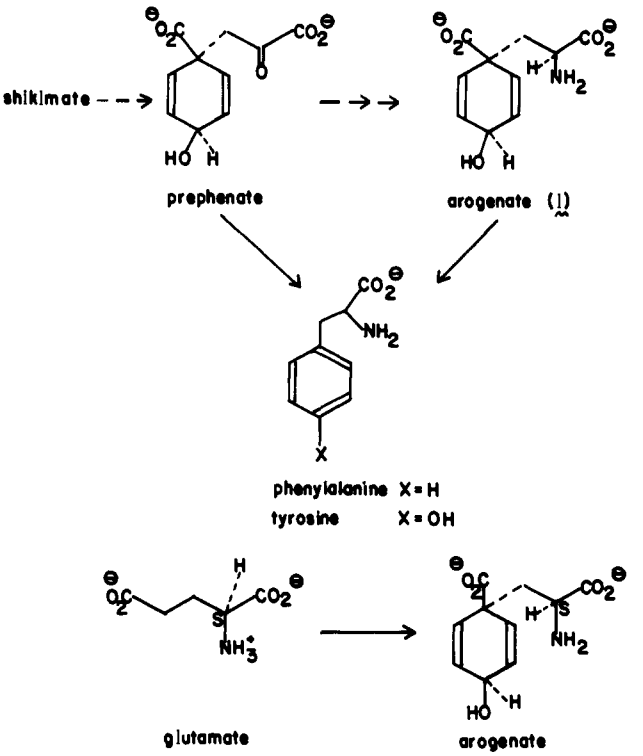
Since its discovery, it had been assumed that prephenic acid, biosynthetically derived from shikimate, was the last nonaromatic intermediate in the elaboration of the crucial amino acids phenylalanine and tyrosine and that these are exclusively derived from the corresponding aryl pyruvates.[1,2] More recently, largely as a consequence of the investigations of the Jensen group,[3,4] an alternative mode of L-tyrosine biosynthesis has been uncovered. The crucial variation is that the transamination of the keto group of prephenate can also occur prior to aromatization. This pathway has been established in a variety of bacterial and yeast organisms.[5,6] Interestingly, in pseudomonal bacteria and plants, both the "prephenate" and the "pretyrosine" routes to tyrosine appear to be cofunctional.[7]

Early investigations delineating the existence of this pathway pointed to the formation of intermediate **1**,[3,4] which was aptly named "pretyrosine". Given its involvement in phenylalanine biosynthesis,[8] the designation pretyrosine has given way[9] to the more general appelation, "arogenate" (**1**). The initial deductions of the structure of arogenate were based more on clever guesswork and intuition than on hard chemical or spectroscopic information. Rigorous investigations into the nature of this curious amino acid were hampered by its instability and extremely difficult accessibility. More recently, very convincing spectroscopic and chiroptical data were brought to bear in support of structure **1** by Zamir and co-workers.[9]



Given its important role in biosynthesis, difficult accessibility, extensive functionality, and precarious stability, a total synthesis of arogenate appeared to be a worthy objective. Particularly interesting to us was the possibility of obtaining the compound in optically pure form. The realization of these goals is the subject of this report. It will be recognized that in this enterprise we were drawing extensively on methodology which previous workers in our laboratory had developed pursuant to the total synthesis of prephenate,[10] as well as of γ-carboxyglutamate[11] and tazettine.[12] Our chiral source was the readily available amino acid, L-glutamic acid in the form of its pyroglutamate derivative **2**.

We have already described[11] the conversion of **2** → **3** in essentially quantitative yield through the agency of the Bredereck reagent, bis(dimethylamino)-*tert*-butoxymethane. Hydrolysis of the enamine linkage was readily accomplished through the action of aqueous 1 N HCl:THF at room temperature, affording **4** as a mixture of geometric isomers.

Reaction of **4** with diphenyl disulfide and tri-*n*-butylphosphine (THF, room temperature)[13] afforded a 68% yield of an *E*/*Z* mixture of vinyl sulfides **5**.[14] These were grouped together for the next step. Oxidation of **5** with *m*-chloroperoxybenzoic acid

(1) Haslam, E. "The Shikimate Pathway"; Wiley: New York, 1974.
(2) For a recent review, see: Ganem, B. *Tetrahedron* **1978**, *34*, 3353.
(3) Stenmark, S. L.; Pierson, D. L.; Glover, G. I.; Jensen, R. A. *Nature (London)* **1974**, *247*, 290.
(4) Fazel, A. M.; Bowen, J.; Jensen, R. A. *Proc. Natl. Acad. Sci. U.S.A* **1980**, *77*, 1270.
(5) (a) Jensen, R. A.; Pierson, D. L. *Nature (London)* **1975**, *254*, 667. (b) Fazel, A. M.; Jensen, R. A. *J. Bacteriol.* **1979**, *138*, 805. (c) *Ibid.* **1979**, *140*, 580.
(6) Bode, R.; Birnbaum, D. *Biochem. Physiol. Pflanzen.* **1978**, *173*, 44.
(7) (a) Patel, N.; Pierson, D. L.; Jensen, R. A. *J. Biol. Chem.* **1977**, *252*, 5839. (b) Patel, N.; Stenmark-Cox, S.; Jensen, R. A. *Ibid.* **1978**, *253*, 2972. (c) Rubin, J. L.; Jensen, R. A. *Plant Physiol.* **1979**, *64*, 727.
(8) See ref 9, footnote 13.
(9) Zamir, L. O.; Jensen, R. A.; Arison, B. H.; Douglas, A. W.; Alberg-Schönberg, G.; Bowen, J. R. *J. Am. Chem. Soc.* **1980**, *102*, 4499.
(10) Danishefsky, S.; Hirama, M.; Fritsch, N.; Clardy, J. *J. Am. Chem. Soc.* **1979**, *101*, 7013.
(11) Danishefsky, S.; Berman, E.; Clizbe, L. A.; Hirama, M. *J. Am. Chem. Soc.* **1979**, *101*, 4385.
(12) Danishefsky, S.; Morris, J.; Mullen, G.; Gammill, R. *J. Am. Chem. Soc.* **1980**, *102*, 2838.
(13) Nakagawa, I.; Hata, T. *Tetrahedron Lett.* **1975**, 1409. For a comparable reaction to prepare selenides, see: Grieco, P. A.; Gilman, S.; Nishizawa, M. *J. Org. Chem.* **1976**, *41*, 1485.
(14) (a) Along with the desired vinyl sulfides **5**, there was isolated a 15.6% yield of the bis sulfide resulting from a 1,4 addition of thiophenol to **5**. (b) **5**: IR ($CHCl_3$) ν_{max} 3.28, 5.61, 5.73, 5.78, 6.18, 7.68 μm; ^1H NMR (250 MHz, $CDCl_3$) δ 2.57 (ddd, $J = 2.4, 3.6, 18.0$ Hz, 1), 2.98 (ddd, $J = 3.0, 10.2, 18.0$ Hz, 1), 4.76 (dd, $J = 3.9, 10.2$ Hz, 1), 5.12 and 5.17 (s, 2 parts of benzylic H, 2), 5.22 and 5.25 (s, 2 parts of benzylic H, 2), 7.3–7.6 (m, 15), 7.66 (dd, $J = 2.4, 3.0$ Hz, 1); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 23.7, 26.8, 47.5, 55.7; 56.8; 58.9; 67.4, 68.3. MS, *m/e* calcd for $C_{27}H_{23}NO_5S$, 473.1297; found, 473.1308.

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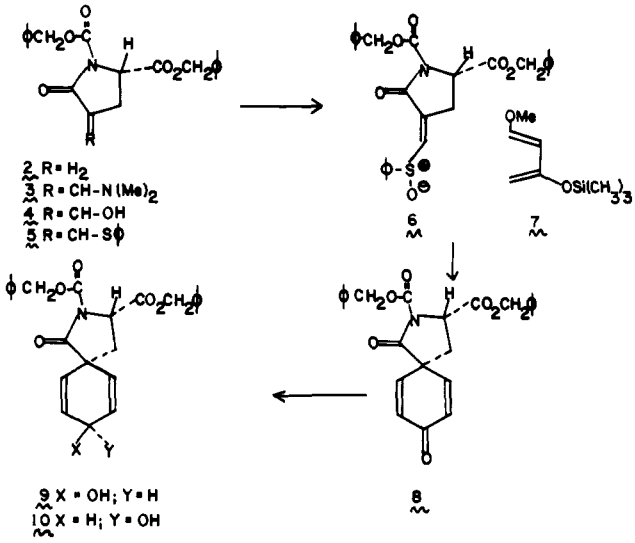
in chloroform at −23 °C for 2.5 h provided a 60% yield of the sulfoxide diastereomers **6**.[15]

Diels–Alder reaction of this glutamate-derived dienophile with diene **7**[16] was carried out in benzene under reflux for 22.5 h. The reaction product was treated with 2.5% acetic acid in ethyl acetate at room temperature for 5 h. Flash chromatography[17] on silica gel afforded a 57% yield of the crystalline dienone, **8**,[18] mp 109.5–111 °C, $[\alpha]_D$ −19.8° (c 1.0, chloroform).

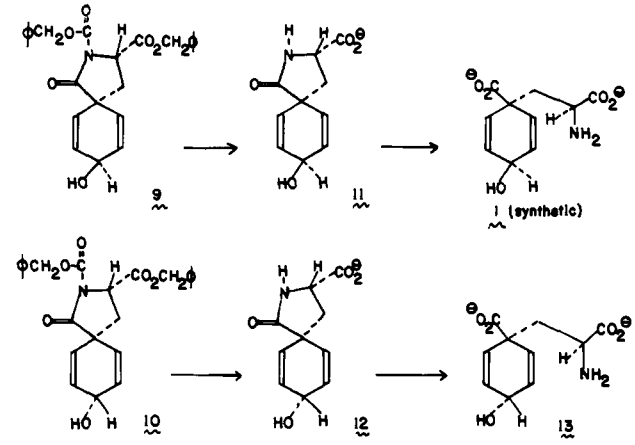
Reduction of the spirodienone with DIBAH in THF–hexane at −78 °C, followed by chromatography on silica gel afforded a 2.4:1 ratio of **9**[19]:**10**[20] (**9**, 56% isolated yield, mp 95.5–97.0° $[\alpha]_D$ −21.2° (c 1.15, chloroform) (**10**, 24% isolated yield, mp 99.5–101 °C, $[\alpha]_D$ −15.4° (c 1.75, chloroform).



Reaction of the major dienol **9** with 2 N sodium hydroxide in methanol (2 mmol of hydroxide/mmol of **9**) at room temperature for 19 h resulted in hydrolysis of the ester and cleavage of the Cbz function. After dilution of the mixture with water, extraction (chloroform) of the benzyl alcohol, and evaporation of the aqueous solution in vacuo, "pyropretyrosine" **11**[21] was obtained in nearly quantitative yield. The susceptibility of this imide-like linkage, such as is present in **9**, to mono deacylation is well precedented from our previous work.[11,22] Similar reaction of dienol **10** afforded epi pyropretyrosine (**12**).[23]

Opening of the lactam function of **11** was achieved with sodium hydroxide in ethanol at 70 °C for 20–48 h.[24a] Evaporation of the volatiles left a residue which contained the desired disodium salt **1**, as well as small amounts of the sodio derivatives of phenylalanine and tyrosine.[24b] Separation was achieved by column chromatography on Sephadex A-25-120 ion exchange resin (HCO_3^- form). Elution with 0.05 M triethylammonium bicarbonate and basification with sodium hydroxide afforded disodium pretyrosinate. *The NMR spectrum* (D_2O, 270 MHz) *of the synthetically derived disodium salt compared closely with a published spectrum at 300 MHz and was identical (save for a few extraneous signals in the naturally derived material) with that obtained* (D_2O, 270 *MHz*) *on our own instrumentation from an authentic specimen kindly furnished by Professor Lolita Zamir.*[25]

In a similar way, the epilactam **12** was converted to the epiarogenate **13**.[26] Its NMR spectrum (D_2O, 270 MHz) while qualitatively very similar to that of **1** is clearly different in its fine details.[27]



The optical rotation of the synthetic disodium salt **1** (10 mg/2mL of 0.1 N NaOH) is $[\alpha]_D$ +6.6°. The $[\alpha]_D$ of the "natural" material has not been reported. That our synthetic material is essentially optically pure is vouchsafed by its transformation to optically pure L-phenylalanine methyl ester, as shown.[28]

(15) (a) We are unsure as to whether the diastereomeric relationship between the two separable isomers is due to the double bond stereochemisty, the chiral sulfur atom, or both. Nevertheless, the dienophile **6** was always submitted to the Diels–Alder reaction as a mixture. (b) **6**: IR (mixture, $CHCl_3$) ν_{max} 5.60, 5.72, 9.50 μm. ^1H NMR (high-R_f isomer, R_f = 0.46, 60% ethyl acetate/hexane, 250 MHz, $CDCl_3$) δ 3.36 (dt, *J* = 2.8, 19.4 Hz, 1), 3.52 (ddd, *J* = 3.1, 9.7, 19.4 Hz, 1), 4.77 (dd, *J* = 3.4, 9.7 Hz, 1), 5.13 (s, 2), 5.22 (s, 2), 7.11 (t, *J* = 2.8 Hz, 1), 7.2–7.6 (m, 15); ^1H NMR (low-R_f isomer, R_f = 0.41, 60% ethyl acetate/hexane, 90 MHz, $CDCl_3$) δ 3.40 (dd, *J* = 3, 7 Hz, 2), 4.76 (t, *J* = 7 Hz, 1), 5.11 (s, 2), 5.20 (s, 2), 7.12 (t, *J* = 3 Hz, 1); 7.2–7.7 (m, 15).

(16) Danishefsky, S.; Kitahara, T.; Yan, C. F.; Morris, J. *J. Am. Chem. Soc.* **1979**, *101*, 6996.

(17) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(18) **8**: IR ($CHCl_3$) ν_{max} 5.50, 5.71, 5.98 μm. ^1H NMR (250 MHz, $CDCl_3$) δ 2.29 (dd, *J* = 3.3, 14.1 Hz, 1), 2.67 (dd, *J* = 9.9, 14.1 Hz, 1); 4.87 (dd, *J* = 3.3, 9.9 Hz, 1), 5.20 (s, 2), 5.27 (s, 2), 6.27 (dd, *J* = 1.6, 9.7 Hz, 1), 6.42 (dd, *J* = 1.6, 9.9 Hz, 1), 6.68 (td, *J* = 2.9, 10.1 Hz, 2), 7.3–7.45 (m, 10). MS *m/e* calcd for $C_{25}H_{21}NO_6$, 431.1369; found, 431.1354.

(19) **9**: R_f = 0.22, 3% methanol/chloroform; IR ν_{max} 2.89, 5.59, 5.78 μm. ^1H NMR (270 MHz, $CDCl_3$) δ 2.15 (dd, *J* = 3.8, 13.9 Hz, 1), 2.41 (dd, *J* = 9.9, 13.9 Hz, 1), 4.40 (m, 1), 4.77 (dd, *J* = 3.8, 9.9 Hz, 1), 5.16 (s, 2), 5.24 (s, 2), 5.68 (br t, *J* = 9.2 Hz, 2); 6.09 (m, 1); 6.22 (m, 1); 7.35 (m, 10); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 35.4, 49.3, 56.4, 61.1, 67.9, 68.9, 151.0, 171.2, 173.0.

(20) **10**: R_f = 0.15, 3% methanol/chloroform; IR ν_{max} 2.80, 5.50, 5.74 μ ^1H NMR (270 MHz, $CDCl_3$) δ 2.16 (dd, *J* = 4.2, 13.9 Hz, 1), 2.47 (dd, *J* = 9.5, 13.9 Hz, 1), 4.69 (m, 1), 4.76 (dd, *J* = 4.2, 9.5 Hz, 1), 5.17 (s, 2), 5.24 (s, 2), 5.63 (br t, *J* = 9.9 Hz, 2), 5.99 (br d, *J* = 10.1 Hz, 1), 6.12 (br d, *J* = 9.7 Hz, 1) 7.35 (m, 10). ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 35.0, 49.3, 56.4, 61.8, 68.1, 69.0, 151.4, 171.3, 172.2.

(21) **11**: IR (KBr) ν_{max} 3.00, 5.93, 6.25, 6.85 μm; ^1H NMR (270 MHz, D_2O, relative to TSP) δ 2.11 (dd, *J* = 6.2, 13.2 Hz, 1), 2.51 (dd, *J* = 8.8, 13.2 Hz, 1), 4.23 (dd, *J* = 6.2, 8.8 Hz, 1), 4.54 (m, 1), 5.77–5.91 (m, 2), 6.03–6.07 (m, 2).

(22) Although treatment of **9** with sodium hydroxide results in selective cleavage of the *N*-Cbz function affording **11**, reaction of **9** with methanol and triethylamine at 70 °Cproceeds to a major extent via the ring-opening mode giving rise to *N*-carbobenzyloxydimethyl pretyrosinate. This latter result is consistent with the cases studied in ref 11.

(23) **12**: IR (KBr) ν_{max} 2.95, 5.97, 6.28, 6.89 μm; ^1H NMR (270 MHz, D_2O, relative to TSP) δ 2.15 (dd, *J* = 6.2, 13.2 Hz, 1), 2.55 (dd, *J* = 8.8, 13.2 Hz, 1), 4.23 (dd, *J* = 6.2, 8.8 Hz, 1), 4.61 (m, 1), 5.73 (d, *J* = 10.3 Hz, 1), 5.81 (d, *J* = 10.3 Hz, 1), 6.01 (d, *J* = 10.3 Hz, 1), 6.02 (d, *J* = 10.3 Hz, 1).

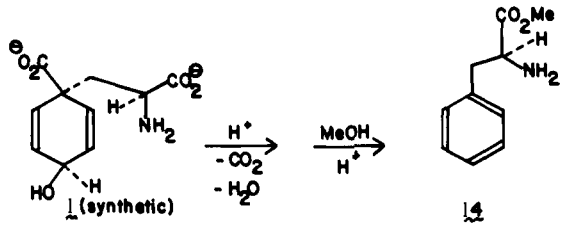
(24) (a) It was discovered that this reaction could be catalyzed by the addition of 1 equiv of sodium carbonate. This improvement resulted in shorter reaction times. (b) The mechanistic origin of the tyrosine from this reaction is not known. Extended reaction times (e.g., 4 days) affords large amounts of tyrosine and much smaller amounts of the desired amino acid **1**. Thus, it appears that the tyrosine is derived directly from the pretyrosine produced in the reaction by an unknown pathway.

(25) Synthetic **1**: IR (KBr) ν_{max} 2.93, 6.33, 6.84 μm; ^1H NMR (270 MHz, D_2O, relative to TSP) δ 1.88 (dd, *J* = 7.0, 13.6 Hz, 1), 2.15 (dd, *J* = 4.9, 13.6 Hz, 1), 3.07 (dd, *J* = 4.9, 7.0 Hz, 1), 4.59 (m, 1); 5.94 (br s, 2), 5.96 (d, *J* = 10 Hz, 1), 6.05 (d, *J* = 10 Hz, 1).

(26) In the case of the *epi*-arogenate **13**, the conversion from **12** to **13** has always been successful; however, we have had difficulties in consistently obtaining pure samples of **13** by using the chromatographic conditions described for isolation of arogenate **1**.

(27) **13**: ^1H NMR (270 MHz, D_2O, relative to TSP) δ 1.93 (dd, *J* = 7.6, 14.0 Hz, 1), 2.22 (dd, *J* = 4.9, 14.0 Hz, 1), 3.15 (dd, *J* = 4.9, 7.6 Hz, 1), 4.55 (m, 1), 5.93 (br s, 2), 5.94 (d, *J* = 9.8 Hz, 1), 6.04 (d, *J* = 9.8 Hz, 1).

(28) The optical purity of **14** was determined by ^1H NMR (270 MHz) to be >95% using the lanthanide shift reagent, tris[3-[(trifluoromethyl)-hydroxymethylene]-*d*-camphorato]europium(III), according to the method of Kainosho. See: Ajisaka, K., Kamisaku, M.; Kainosho, M. *Chem. Lett.* **1972**, 857.



The total synthesis of optically pure arogenate from glutamate has thus been achieved. Furthermore, it appears that in this case, synthesis surpasses isolation in providing access to reasonable amounts of homogeneous material. It is hoped and expected that this synthesis will be helpful in designing experiments addressed to understanding the arogenate biosynthetic pathway.

Acknowledgment. This research was supported by P.H.S. Grant AI 16943-01. NMR measurements at 250 MHz were obtained on facilities supported by P.H.S. Grant RR-00296-11 for the Mellon Institute, Pitt, Carnegie (M.P.C.) Corporation. Those at 270 MHz were obtained through the auspices of the Northeast Regional N.S.F/N.M.R. Facility at Yale University supported by the N.S.F. Chemistry Division Grant C.H.F. 7916210. Additional support was forthcoming through an Andrew Mellon Predoctorial Fellowship to J.M. and an N.I.H. Postdoctoral Fellowship 06196-02 to L.A.C. The advice and encouragement of Professor Lolita Zamir of the State University of New York at Binghamton and the receipt from her of an authentic specimen sample of arogenate are gratefully acknowledged. We also acknowledge the valuable advice of Professor John Gerlt of Yale University in dealing with the chromatographic purification of synthetic arogenate.

(Trimethylsilyl)cyclopentene Annulation: A Regiocontrolled Approach to the Synthesis of Five-Membered Rings

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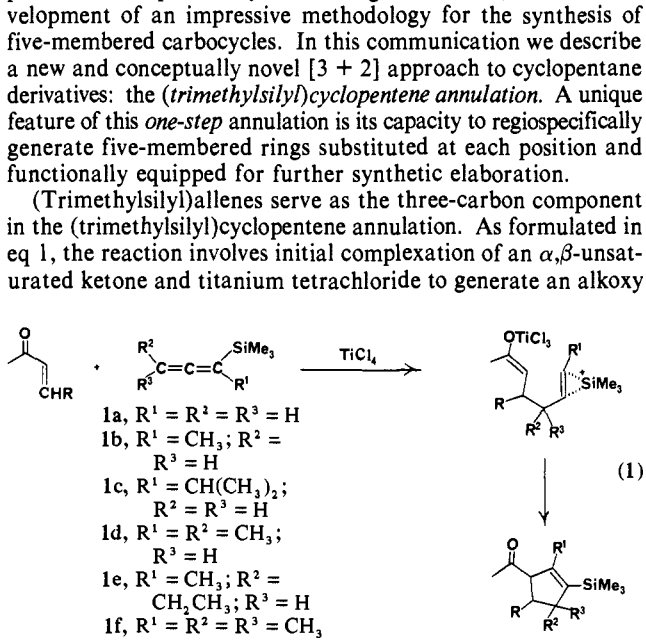
The identification of the prostaglandins and polyquinane natural products as important synthetic targets has stimulated the development of an impressive methodology for the synthesis of five-membered carbocycles. In this communication we describe a new and conceptually novel [3 + 2] approach to cyclopentane derivatives: the *(trimethylsilyl)cyclopentene annulation.* A unique feature of this *one-step* annulation is its capacity to regiospecifically generate five-membered rings substituted at each position and functionally equipped for further synthetic elaboration.

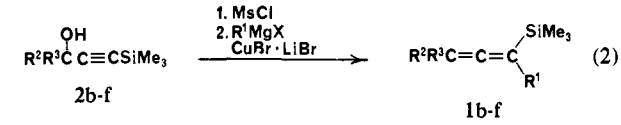
(Trimethylsilyl)allenes serve as the three-carbon component in the (trimethylsilyl)cyclopentene annulation. As formulated in eq 1, the reaction involves initial complexation of an α,β-unsaturated ketone and titanium tetrachloride to generate an alkoxy allylic carbocation. Regiospecific electrophilic substitution[1,2] of this cation at C_3 of the (trimethylsilyl)allene[3] provides a vinyl cation stabilized by interaction with the adjacent carbon–silicon bond. A 1,2 shift of the trimethylsilyl group[4,5] then affords an isomeric vinyl cation which is intercepted by the titanium enolate to produce a new five-membered ring.



1a, $R^1 = R^2 = R^3 = H$
1b, $R^1 = CH_3$; $R^2 = R^3 = H$
1c, $R^1 = CH(CH_3)_2$; $R^2 = R^3 = H$
1d, $R^1 = R^2 = CH_3$; $R^3 = H$
1e, $R^1 = CH_3$; $R^2 = CH_2CH_3$; $R^3 = H$
1f, $R^1 = R^2 = R^3 = CH_3$

(1)

The requisite 1-substituted (trimethylsilyl)allenes **1b–f** are easily obtained with a variety of substitution patterns employing the method of Westmijze and Vermeer (eq 2).[6,7] (Trimethylsilyl)-



(2)

allene itself is most conveniently prepared with the use of our previously reported procedure.[2a]

Table I delineates the scope of the (trimethylsilyl)cyclopentene annulation. In a typical reaction, 1.5 equiv of distilled titanium tetrachloride was rapidly added to a solution of methyl vinyl ketone and 1.0 equiv of allene **1b** in methylene chloride at −78 °C. The resulting red solution was stirred at −78 °C for 1 h, and the reaction was then quenched by addition of water and ether. Ether extraction furnished the (trimethylsilyl)cyclopentene **3**, obtained in 68–75% yield after chromatographic purification. The structure of the annulation product was established by spectral characterization[8] and conversion to 1-acetyl-2-methylcyclopentene.[9]

This last reaction illustrates the useful transformation of the annulation products to α,β-unsaturated ketones. Exposure of the (trimethylsilyl)cyclopentenes to either potassium carbonate in methanol or a dilute solution of hydrofluoric acid in acetonitrile at 25 °C results in isomerization followed by desilylation of the intermediate γ-trimethylsilyl α,β-unsaturated ketones. The vinylsilane moiety should serve as the basis for a variety of other interesting synthetic transformations of the initial annulation products.[1,10]

Both cyclic and acyclic enones participate in the (trimethylsilyl)cyclopentene annulation. α-Methylene ketones react to form spiro-fused systems. Molecular models indicate that the intermediates derived from acetylcyclohexene, cyclohexenone, and cyclopentenone are constrained to cyclize to cis-fused adducts.[11,12]

(1) For a review of electrophilic substitution of organosilicon compounds, see: Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761.

(2) For previous examples of electrophilic substitution of (trimethylsilyl)allenes, see: (a) Danheiser, R. L.; Carini, D. J. *J. Org. Chem.* **1980**, *45*, 3925. (b) Bourgeois, P.; Calas, R.; Merault, G. *J. Organomet. Chem.* **1977**, *141*, 23. Bourgeois, P. *C. R. Hebd. Seances Acad. Sci., Ser. C.* **1974**, *278*, 969. (c) Jellal, A.; Santelli, M. *Tetrahedron Lett.* **1980**, 4487.

(3) The C–Si bond in (trimethylsilyl)allenes is oriented cis coplanar to only the *allylic* π bond and thus can only afford direct stabilization to the transition state resulting from electrophilic substitution at C_3.

(4) For a review of 1,2-cationic rearrangements in organosilicon compounds, see: Brook, A. G.; Bassindale, A. R. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. II, pp 190–192.

(5) For a review of migration across the double bond of vinyl cations, see: Stang, P. J.; Rappaport, Z.; Hanack, M.; Subramanian, L. R. "Vinyl Cations"; Academic Press: New York, 1979; pp 459–483.

(6) Westmijze, H.; Vermeer, P. *Synthesis* **1979**, 390. We thank James T. Kadonaga for assistance in the preparation of these allenes.

(7) (Trimethylsilyl)propargylic alcohols **2d–f** were prepared by addition of (trimethylsilyl)acetylide to the requisite aldehydes and ketones.

(8) IR (film) 2957, 2910, 2850, 1708, 1615, 1350, 1250, 835 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 0.06 (s, 9 H), 1.67 (m, 3 H), 2.00 (s, 3 H), 1.79–2.08 (m, 2 H), 2.33–2.58 (m, 2 H), 3.39 (t, 1 H, J = 7 Hz); mass spectrum *m/e* 196.1284 (M^+).

(9) Semicarbazone mp 220–220.5 °C, lit. mp 220–221 °C: Tabushi, I.; Fujita, K.; Oda, R. *Tetrahedron Lett.* **1968**, 4247.

(10) For a review of the chemistry of vinylsilanes, see: Fleming, I. In "Comprehensive Organic Chemistry"; Jones, D. N., Ed.; Pergamon Press: Oxford, 1979; Vol. 3, pp 608–662.

(11) The coupling constants for the ring fusion protons in hydrindanes **4**, **13**, **16**, and **17** (J = 6.2–7.3 Hz) and bicyclo[3.3.0]octanes **7**, **19**, and **20** (J = 7.3–8.1 Hz) support the assignment of cis ring fusion stereochemistry in these compounds.[13]

(12) Epimerization of the kinetic products would not be expected to occur without significant isomerization to conjugated enones.[13]

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