Experimental Section

Melting points and boiling points are uncorrected. Elemental analyses were performed by Mr. J. Nemeth and associates.

The reactants **1**, **2**, **3**, **4**, **5**, and **6** were analytically pure materials which had physical properties, infrared spectra, and nuclear magnetic resonance spectra consistent with the assigned structures.[14] All materials are liquids except **5**. *Methyl fluorosulfonate is reported to be very toxic and should be handled with appropriate caution;*[15] it (Aldrich) was distilled and stored in a dry argon atmosphere at −15 °C.

***N,N*-Dimethyl-*O*-methylbenzimidatium fluorosulfate** was prepared from separate reactions of **1** and **2** with excess methyl fluorosulfonate in ethylene dichloride. Removal of the solvent and excess methylating agent in vacuo gave quantitative yields: mp 95–98 °C; NMR (acetonitrile-d_3) δ 7.70 (ArH), 3.90 (OCH_3), 3.42, 3.13 [$N(CH_3)_2$]; IR (Nujol) 1610, 1600, 1510 cm^{-1};[16] combustion analysis, Table III.

***N,N*-Dimethyl-*O*-methylacetimidatium fluorosulfonate** was prepared by a procedure similar to that used above from **3** and from **4**: mp 117–120 °C; NMR (acetonitrile-d_3) δ 4.00 (OCH_3), 3.18, 3.07 [$N(CH_3)_2$], 2.35 (CCH_3); IR (Nujol) 1680 cm^{-1};[16] combustion analysis, Table III.

***N,N*-Dimethyl-*S*-methylthiobenzimidatium fluorosulfonate** was prepared by a procedure similar to that used above from **5** and from **6**: mp 103–106 °C; NMR (Me_2SO-d_6) δ 7.33 (ArH), 3.55, 3.20 [$N(CH_3)_2$], 2.17 (SCH_3); IR (Nujol) 1616, 1269, 1068, 774 cm^{-1};[16] combustion analysis, Table III.

Heats of methylation and vaporization for 1–6 and the heat of fusion of 5 were determined by the techniques previously described.[2] The only detectable products from the calorimetric runs were the fluorosulfonate salts. The salts were isolated and shown to be virtually identical with authentic material by IR and NMR criteria.

Acknowledgment. We are grateful to the National Science Foundation for support of this work.

Registry No.—Methyl fluorosulfonate, 421-20-5.

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Modified Cephalosporins: Synthesis of Benzo[3,4]cephams[1]

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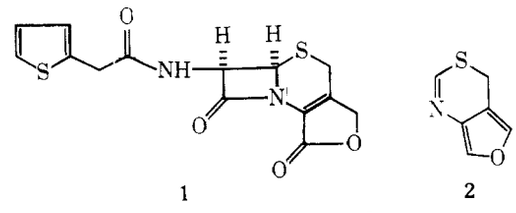
A synthetic route to a benzo[3,4]cepham system is described. The key step of the synthesis involved treatment of the novel 7-*tert*-butoxycarbonyl-4*H*-benzo-3,1-thiazine (**4**) with azidoacetyl chloride and triethylamine to furnish the *trans*-β-lactam **13a**. Conversion of **13a** to the cephalosporin analogue **17** followed established synthetic methodology.

A novel totally synthetic route to (±)-desacetylcephalothin lactone (**1**) was recently reported from our laboratories, the key step being the reaction of azidoacetyl chloride/triethylamine with the novel 4*H*-furo[3,4-*d*]-1,3-thiazine (**2**) to give the furo[3,4]cephams **3**.[3] This paper describes the synthesis of benzo[3,4]cephams via the new thiazine **4**.



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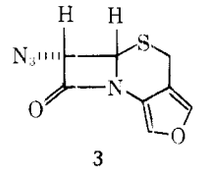
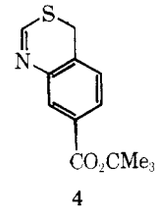
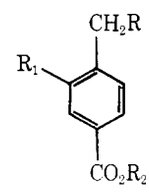


3



4

Reaction of 4-bromomethylbenzoic acid (**5**) with nitric acid gave the 3-nitro compound **6**, which was converted into the *tert*-butyl ester **7**. Silver perchlorate promoted hydrolysis of



5, R = Br; $R_1 = R_2 = H$
6, R = Br; $R_1 = NO_2$; $R_2 = H$
7, R = Br; $R_1 = NO_2$; R_2 = *tert*-butyl
8, R = OH; $R_1 = NO_2$; R_2 = *tert*-butyl
9, R = OH; $R_1 = NH_2$; R_2 = *tert*-butyl
10, R = OH; R_1 = NHCHO; R_2 = *tert*-butyl
11, R = OCHO; R_1 = NHCHO; R_2 = *tert*-butyl
12, R = Cl; R_1 = NHCHO; R_2 = *tert*-butyl

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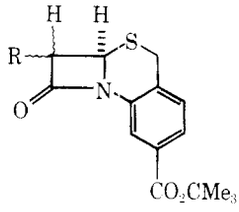
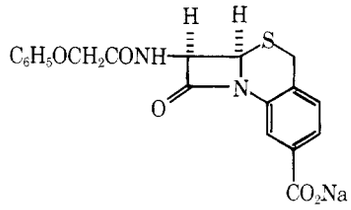
7 furnished the alcohol **8**, which was hydrogenated (5% Pt/C) to amine **9**. Attempts to prepare the *N*-formylcarbinol **10** by selective N-formylation failed. However, **9** was readily transformed into a mixture of **10** and *O,N*-diformate **11** by reaction with formic acetic anhydride in pyridine. Treatment with ammonia caused selective hydrolysis of the *O*-formate group to give **10** in 56% yield from **8**.

The next stage of the synthesis required the transformation of the *N*-formylcarbinol **10** into a thioformate derivative bearing chlorine on the benzylic carbon since previous experience indicated that this compound would cyclize directly to thiazine **4**.[3] Accordingly, **10** was transformed into the benzylic chloride **12** by reaction with triphenylphosphine/carbon tetrachloride[4] and this substance in turn treated with P_4S_{10}. The resulting product, formulated as thiazine **4** rather than the thioformate, was unstable in the solid state and polymerized ($t_{1/2} \sim 15$ min) to a material insoluble in organic solvents. However, solutions of **4** could be kept for several days without deterioration. Its NMR spectrum showed a 2-H singlet at 3.93 ppm for the methylene protons and a 1-H singlet at 7.45 ppm for the vinyl proton on the thiazine ring, as well as the expected resonances for the *tert*-butyl and three aromatic protons.

Because of the instability of the benzothiazine **4** it was necessary to treat solutions of **4**, obtained directly from the P_4S_{10} reaction, with azidoacetyl chloride/triethylamine in order to form the β-lactam system.[5] This afforded the expected *trans*-β-lactam **13a** in 60% yield from **12**. The trans





a, *trans*-6,7-H; b = *cis*-6,7-H **17**

13a, R = N_3
14a,b, R = NH_2
15a,b, R = *p*-$NO_2C_6H_4CH{=}N$
16a,b, R = $C_6H_5OCH_2CONH$

stereochemistry in **13a** follows from the 2.2-Hz coupling constant for the 6 and 7 protons, which is in agreement with literature values reported for analogous systems.[6]

The conversion of the 7α-azido-*trans*-cepham **13a** into the 7β-amino cis series was accomplished as follows. Azide **13a** was reduced with aqueous $(NH_4)_2S$[3] to the amine **14a**, which was converted into the Schiff's base **15a** with *p*-nitrobenzaldehyde. Equilibration of **15a** with diisopropylethylamine produced a 1:5 mixture of the *cis*- and *trans*-*p*-nitrobenzylidene derivatives **15b** and **15a**, respectively.[7] Fractional crystallization provided in ~75% yield the starting trans isomer **15a** and the cis isomer **15b** (~10% yield) admixed with ca. 10% of **15a**.

Hydrolysis of the *p*-nitrobenzylidene group of **15b** gave the *cis*-amine **14b**, which was treated directly with phenoxyacetyl chloride to give **16b**. The cis arrangement of the β-lactam protons in **16b** (and also in **14b** and **15b**) was confirmed by the expected 4.5-Hz coupling constant for the 6- and 7-H signals.[6] For preparative purposes it proved to be most convenient to reequilibrate the recovered trans Schiff's base **15a** several times and then to process the combined fractions enriched in the cis isomer as before. This provided a 1:3 mixture of the *cis*- and *trans*-7-phenoxyacetamido esters **16b** and **16a**, respectively, which was then separated chromatographically.

Transformation of the *cis*-*tert*-butyl ester **16b** into the amorphous sodium salt **17** was accomplished following established methodology. Salt **17** showed no antibacterial activity in vitro at a concentration of 100 μg/mL against a variety of gram-positive and -negative organisms.

Experimental Section

Melting points are uncorrected. Infrared spectra were measured as KBr disks on a Perkin-Elmer 237B spectrometer. NMR spectra were obtained with Varian A-60 and HA-100 instruments using ca. 5% w/v solutions in $CDCl_3$. Chemical shifts are given in ppm from Me_4Si. Elemental analyses were performed by the Analytical Department at Syntex Research.

3-Nitro-4-bromomethylbenzoic Acid (6). 4-Bromomethylbenzoic acid (**5**; 2 g, 9.3 mmol) was added slowly with stirring to fuming nitric acid (10 mL) at −10 to −20 °C. After 0.5 h the reaction mixture was poured into ice water, and the crystalline product was collected and dried to yield 1.8 g (74%) of **6**, mp 93–94 °C (from $CHCl_3$/hexane).

Anal. Calcd for $C_8H_6BrNO_4$: C, 36.95; H, 2.33; N, 5.39; Br, 30.73. Found: C, 37.00; H, 2.29; N, 5.18; Br, 30.57.

***tert*-Butyl 3-Nitro-4-bromomethylbenzoate (7).** A solution of the acid **6** (2 g, 8.7 mmol), glyme (3 mL), isobutylene (ca. 15 g), and concentrated H_2SO_4 (0.2 mL) was heated in an autoclave at 50 °C for 18 h. After cooling with dry ice the reaction mixture was diluted with CH_2Cl_2 (100 mL), and the resulting solution was washed with 10% Na_2CO_3 (4 × 15 mL) and H_2O (to neutral), dried (Na_2SO_4), and evaporated to give **7** (2.1 g, 72%), mp 64 °C (from Et_2O/hexane).

Anal. Calcd for $C_{12}H_{14}NO_4Br$: C, 45.59; H, 4.46; N, 20.24; Br, 25.28. Found: C, 45.21; H, 4.38; N, 20.14; Br, 24.89.

***tert*-Butyl 3-Nitro-4-hydroxymethylbenzoate (8).** A solution of the ester **7** (0.32 g, 1 mmol) in acetone (5 mL) was stirred for 48 h at 20 °C with a solution of $AgClO_4$ (0.4 g, 1.9 mmol) dissolved in water (2.5 mL). The reaction mixture was filtered, and the bulk of the acetone was evaporated under reduced pressure. Ether (100 mL) was added, and the resulting solution was washed with H_2O (3 × 25 mL) and brine (1 × 25 mL), dried (Na_2SO_4), and evaporated. The residue was dissolved in EtOAc and filtered through a column of SiO_2 (5 g) to yield after evaporation of the solvent the hydroxymethyl derivative **8** (0.2 g, 77%): mp 73–74 °C (Et_2O/hexane); NMR 1.61 (s, *tert*-butyl H's), 5.08 (s, CH_2OH), 7.90 (d, J = 8 Hz, 5-H), 8.28 (dd, J = 2, 8 Hz, 6-H), 8.68 ppm (d, J = 2 Hz, 2-H).

Anal. Calcd for $C_{12}H_{15}NO_5$: C, 56.91; H, 5.97; N, 5.53. Found: C, 57.16; H, 6.03; N, 5.14.

***tert*-Butyl 3-Formamido-4-hydroxymethylbenzoate (10).** A solution of the nitro compound **8** (1.27 g, 5 mmol) in EtOH (25 mL) was hydrogenated over 5% Pd/C (0.05 g) until the uptake of hydrogen ceased (ca. 4 h). The catalyst was removed by filtration, and the alcohol was evaporated under reduced pressure to afford the crude amine **9** as an oil, which was dissolved in pyridine (8 mL) and treated with a solution of formic acetic anhydride (2 mL) in pyridine (4 mL). After keeping it at 0 °C for 18 h, the reaction mixture was evaporated to dryness, dissolved in MeOH (40 mL), and treated with several drops of MeOH saturated with NH_3. After TLC examination revealed that hydrolysis of the diformate was complete (ca. 5 h), the MeOH was evaporated and the residue was dissolved in EtOAc and filtered through a short column of SiO_2 (15 g). After evaporation of the combined eluates the residue was crystallized from Et_2O/petroleum ether to yield **10** (0.7 g, 56% from **8**), mp 128–129 °C.

Anal. Calcd for $C_{13}H_{17}NO_4$: C, 62.14; H, 6.82; N, 5.57. Found: C, 62.26; H, 6.74; N, 5.44.

***tert*-Butyl 3-Formamido-4-chloromethylbenzoate (12).** A solution of alcohol **10** (2.5 g, 10 mmol) in dry DMF (40 mL) was treated with $(C_6H_5)_3P$ (3.95 g, 15 mmol) and CCl_4 (2.15 g, 14 mmol) and then heated to 50 °C for 0.5 h. The solvent was evaporated under reduced pressure, and the residue was dissolved in CH_2Cl_2 and adsorbed on a column of SiO_2 (70 g). Elution with CH_2Cl_2 and mixtures of CH_2Cl_2/EtOAc (9:1 and 4:1) gave **12** mixed with $(C_6H_5)_3PO$. Rechromatography on SiO_2 (80 g) and slow elution with CH_2Cl_2 gave a series of fractions which were combined and crystallized from Et_2O/hexane to furnish **12** (1.55 g, 58%), mp 89–90 °C.

Anal. Calcd for $C_{13}H_{16}NO_3Cl$: C, 57.88; H, 5.98; N, 5.19; Cl, 13.16. Found: C, 57.50; H, 5.81; N, 5.22; Cl, 12.93.

7-*tert*-Butoxycarbonyl-4*H*-benzo-3,1-thiazine (4). A solution of **12** (1.08 g, 4 mmol) in dry THF (100 mL) was stirred with P_4S_{10} (1.6 g, 7.5 mmol) at 45 °C for 0.5 h. The reaction mixture was cooled and stirred briefly with 10% aqueous NaOH (50 mL). The organic phase was separated, diluted with CH_2Cl_2 (100 mL), washed with saturated NaCl (2 × 50 mL), and dried (Na_2SO_4). Since **4** polymerized rapidly in the solid state, the foregoing CH_2Cl_2 solution was evaporated to a volume of 60 mL by distillation under reduced pressure and used

immediately in the next reaction: NMR 1.58 (s, *tert*-butyl H's), 3.93 (s, CH_2S), 7.1 (d, J = 8.5 Hz, 5-H), 7.88 (dd, J = 2, = 8.5 Hz, 6-H), 7.95 (d, J = 2 Hz, 8-H), 8.45 ppm (s, 2-H).

(±)-7α-Azido-3c-*tert*-butoxycarbonylbenzo[3,4]cepham (13a). The foregoing solution of **4** was treated sequentially with Et_3N (1.73 g, 17.3 mmol) and a solution of azidoacetyl chloride (1.5 g, 12 mmol) in CH_2Cl_2 (30 mL) in five portions over a 1-h period in a N_2 atmosphere. After 1 h the reaction mixture was washed with saturated NaCl (2 × 40 mL), dried (Na_2SO_4), and evaporated. The crude product was dissolved in CH_2Cl_2 and filtered through SiO_2 (25 g) to yield **13a** (0.8 g, 60% from **12**): mp 113–114 °C (Et_2O/hexane); IR 2130, 1775, 1710 cm^{-1}; NMR 1.61 (s, *tert*-butyl H's), 3.88, 4.13 (AB q, J = 17 Hz, CH_2S), 4.78 (d, J = 2.2 Hz, 7-H), 4.94 (d, J = 2.2 Hz, 6-H), 7.25 (d, J = 8 Hz, 3a-H), 7.76 (dd, J = 2, 8 Hz, 3b-H), 8.32 ppm (d, J = 2 Hz, 3d-H).

Anal. Calcd for $C_{15}H_{16}N_4O_3S$: C, 54.20; H, 4.85; N, 16.86; S, 9.65. Found: C, 54.45; H, 4.87; N, 16.70; S, 9.27.

(±)-7α-Amino-3c-*tert*-butoxycarbonylbenzo[3,4]cepham (14a) and 7α-Phenoxyacetamide Derivative 16a. A solution of lactam **13a** (0.33 g, 1 mmol) in MeOH (15 mL) was stirred with 22% aqueous $(NH_4)_2S$ (1 mL, ~3 mmol) at 20 °C for 20 min. The reaction mixture was concentrated to ca. 7 mL under reduced pressure, diluted with CH_2Cl_2 (50 mL), washed with saturated NaCl (2 × 25 mL), dried (Na_2SO_4), and evaporated to yield the amine **14a** (0.13 g) as an oil: NMR 1.61 (s, *tert*-butyl H's), 3.71, 4.08 (AB q, J = 16.5 Hz, CH_2S), 4.36 (d, J = 2 Hz, 6-H), 4.80 (d, J = 2 Hz, 7-H), 7.18 (d, J = 8 Hz, 3a-H), 7.63 (dd, J = 2, 8 Hz, 3b-H), 8.25 ppm (d, J = 2 Hz, 3d-H).

The treatment of amine **14a** (0.1 g, 0.33 mmol) in CH_2Cl_2 (4 mL) containing Et_3N (2 drops) with phenoxyacetyl chloride (0.06 g, 0.36 mmol) for 18 h followed by addition of H_2O and isolation with CH_2Cl_2 gave **16a:** mp 173–174 °C (EtOAc/hexane); IR 3450, 2980, 1775, 1715, 1435 cm^{-1}; NMR 1.62 (s, *tert*-butyl H's), 3.77, 4.10 (AB q, J = 17 Hz, CH_2S), 4.56 (s, CH_2O), 5.14 (d, J = 2 Hz, 6-H), 5.08 (dd, J = 2, 8 Hz, 7-H), 6.94 (d, J = 8 Hz, 3a-H), 7.63 (dd, J = 2, 8 Hz, 3b-H), 8.34 ppm (d, J = 2 Hz, 3d-H).

Anal. Calcd for $C_{23}H_{24}N_2O_5S$: C, 62.71; H, 5.49; N, 6.36; S, 7.28. Found: C, 62.90; H, 5.78; N, 6.20; S, 6.85.

***p*-Nitrobenzylidene Schiff's Base 15a of (±)-7α-Amino-3c-*tert*-butoxycarbonylbenzo[3,4]cepham (14a).** A solution of the crude amine **14a** (0.3 g, 1 mmol) in benzene (50 mL) containing *p*-nitrobenzaldehyde (0.16 g, 1.05 mmol) was stirred with anhydrous $MgSO_4$ (1.2 g) for 18 h. The salt was filtered off and washed with benzene, and the combined filtrates were evaporated to dryness. The residue was twice crystallized from EtOH to yield **15a:** mp 187–193 °C dec; IR 3450, 3000, 1770, 1710, 1380, 1110 cm^{-1}; NMR, 1.61 (s, *tert*-butyl H's), 3.86, 4.14 (AB q, J = 17 Hz, CH_2S), 5.03 (dd, J = 2, 2 Hz, 7-H), 5.24 (d, J = 2 Hz, 6-H), 7.26 (d, J = 8 Hz, 3a-H), 7.70 (dd, J = 2, 8 Hz, 3b-H), 7.97, 8.27 (AA'BB' pattern, *p*-$NO_2C_6H_4$), 8.32 (d, J = 2H, 3d-H), 8.65 ppm (broad, CH=N). This substance failed to give a satisfactory elemental analysis.

Equilibration of the Schiff's Base 15a. A solution of the Schiff's base **15a** (0.66 g, 1.5 mmol) in THF (35 mL) was cooled to 0 °C and treated with *i*-Pr_2NEt (1 mL) in a N_2 atmosphere. After 1 h the reaction mixture was diluted with benzene (200 mL), washed with H_2O (2 × 100 mL), 0.1 N HCl (2 × 100 mL), H_2O (2 × 100 mL), pH 8 phosphate/citrate buffer (2 × 100 mL), and saturated NaCl (2 × 100 mL), dried ($MgSO_4$), and evaporated to give a 1:4 mixture of **15b** and **15a**, respectively, as an oil. Recrystallization of this product from EtOH gave the starting **15a** (0.49 g) and a second crop (0.065 g) consisting of a 9:1 mixture of **15b** and **15a**, respectively.

(±)-7β-Phenoxyacetamido-3c-*tert*-butoxycarbonylbenzo[3,4]cepham 16b. A solution of the second crop of material (0.065 g, 0.15 mmol) from the preceding experiment in $CHCl_3$ (0.5 mL) was added with stirring to a solution of dinitrophenylhydrazone (DNPH; 0.035 g, 0.175 mmol) and *p*-TsOH·H_2O (0.035 g, 0.175 mmol) in EtOH (3 mL). After 45 min the reaction mixture was filtered and the collected precipitate washed with EtOH (2 × 5 mL). The filtrate was evaporated to dryness under reduced pressure, and the resulting residue was dissolved in Et_2O (50 mL) and washed with pH 8 phosphate/citrate buffer (20 mL). The Et_2O layer was dried over $MgSO_4$ and evaporated to yield the crude amine **14b** (0.05 g, 0.16 mmol), which was dissolved in CH_2Cl_2 (3 mL) containing 1 drop of Et_3N and treated with phenoxyacetyl chloride (0.03 g, 0.18 mmol). After 18 h the reaction mixture was worked up by addition of H_2O and isolation with CH_2Cl_2 to afford **16b** (0.065 g): mp 228–229 °C (EtOAc/hexane); IR 3290, 3250, 3100, 1780, 1705, 1675, 1555, 1430 cm^{-1}; NMR 1.62 (s, *tert*-butyl H's), 3.80, 4.10 (AB q, J = 17 Hz, CH_2S), 4.57 (s, CH_2O), 5.28 (d, J = 4.5 Hz, 6-H), 5.92 (dd, J = 4.5, 9 Hz, 7-H), 6.92 (d, J = 8 Hz, 3a-H), 7.69 (dd, J = 2, 8 Hz, 3b-H), 7–7.4 (m, C_6H_5O), 8.15 ppm (d, J = 2 Hz, 3d-H).

Anal. Calcd for $C_{23}H_{24}N_2O_5S$: C, 62.71; H, 5.49; N, 6.36; S, 7.28. Found: C, 63.02; H, 5.40; N, 6.19; S, 7.35.

Sodium (±)-7β-Phenoxyacetamidobenzo[3,4]cepham-3c-carboxylate (17). The *cis-tert*-butyl ester **16b** (0.022 g, 50 μmol) was dissolved in cold trifluoroacetic acid (TFA; 0.6 mL), and this solution was kept at 0 °C for 5 min. The solvent was removed under reduced pressure, the residue was dissolved in THF (2 mL), and a solution of $NaHCO_3$ (0.005 g, 60 μmol) in H_2O (0.5 mL) was added. The resulting solution was evaporated to dryness under reduced pressure to afford the sodium salt **17** (~0.026 g) as an amorphous solid: IR ($CHCl_3$) 3300, 3000, 1777, 1695, 1675, 1535, 1440, 1210 cm^{-1}; NMR (Me_2SO-d_6) 3.97, 4.18 (AB q, J = 16 Hz, CH_2S), 4.62 (s, CH_2O), 5.33 (d, J = 4.5 Hz, 6-H), 5.72 (d, J = 4.5 Hz, 7-H), 6.96–7.40 (m, C_6H_5O and 3b-H), 7.62 (dd, J = 2, 8 Hz, 3a-H), 8.05 ppm (d, J = 2 Hz, 3d-H).

(±)-7β-Phenoxyacetamido-3c-*tert*-butoxycarbonylbenzo[3,4]cepham (16b) by Multiple Reequilibration of Recovered Schiff's Base 15a. A solution of the Schiff's base **15a** (0.49 g, 1.1 mmol) in THF (26 mL) was cooled to 0 °C and treated with *i*-Pr_2NEt (0.74 mL) in a N_2 atmosphere. After 1 h the reaction mixture was processed as described previously, the crude product crystallizing from EtOH to give **15a** (0.33 g) and second (0.04 g), third (0.05 g), and mother liquor (0.04 g) fractions consisting of mixtures of **15a** and **15b**. The recovered **15a** was reequilibrated and fractionated by crystallization four more times, and the second, third, and mother liquor fractions were combined to yield 0.42 g of a 2–3:1 mixture of **15a** and **15b**, respectively. This mixture was hydrolyzed as before with DNPH and *p*-TsOH followed by acylation with phenoxyacetyl chloride to produce roughly a 1:3 mixture of **16b** and **16a**, respectively. Crystallization from EtOAc/hexane furnished **16b** (0.035 g), mp 228–229 °C, a second crop consisting of a 1:3 mixture of **16a** and **16b**, respectively, and a third crop of **16a** (ca. 90% pure by TLC). The second crop of material was separated by chromatography over SiO_2 (20 g) eluting with hexane/EtOAc (75:35) to yield, after combination of the appropriate fractions, pure samples of **16a** (0.12 g), mp 167–168 °C (EtOAc/hexane), and **16b** (0.045 g), mp 228–229 °C (EtOAc/hexane), identical in all respects with samples obtained as described in earlier experiments.

Registry No.—**4**, 65276-89-3; **5**, 6232-88-8; **6**, 55715-03-2; **7**, 65276-90-6; **8**, 65276-91-7; **9**, 65276-92-8; **10**, 65276-93-9; **12**, 65276-94-0; **13a**, 65276-95-1; **14a**, 65276-96-2; **14b**, 65276-97-3; **15a**, 65276-98-4; **15b**, 65276-99-5; **16a**, 65277-00-1; **16b**, 65277-01-2; **17**, 65277-02-3; isobutylene, 115-11-7; formic acetic anhydride, 2258-42-6; P_4S_{10}, 12066-62-5; azidoacetyl chloride, 30426-58-5; phenoxyacetyl chloride, 701-99-5; *p*-nitrobenzaldehyde, 555-16-8.

References and Notes

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