crotyl bromide, 4784-77-4; *N*-methyl-*p*-toluidine, 623-08-5; *N*-methyl-*N*-*n*-butyl-*p*-toluidine, 57049-30-6; *n*-butyl bromide, 109-65-9; peracetic acid, 79-21-0; (−)-*O,O*-dibenzoyltartaric acid, 2743-38-6; (*R,R*)-*O,O*-dibenzoylpertartaric acid, 57049-31-7; potassium diazocarbonate, 4910-62-7; (*S*)-(+)-2-butanol, 4221-99-2.

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Self-Immolative Asymmetric Synthesis. II. Transfer of Chirality from Tetrahedral Carbon to Trigonal Carbon in Chiral Amine Oxide Rearrangement[1]

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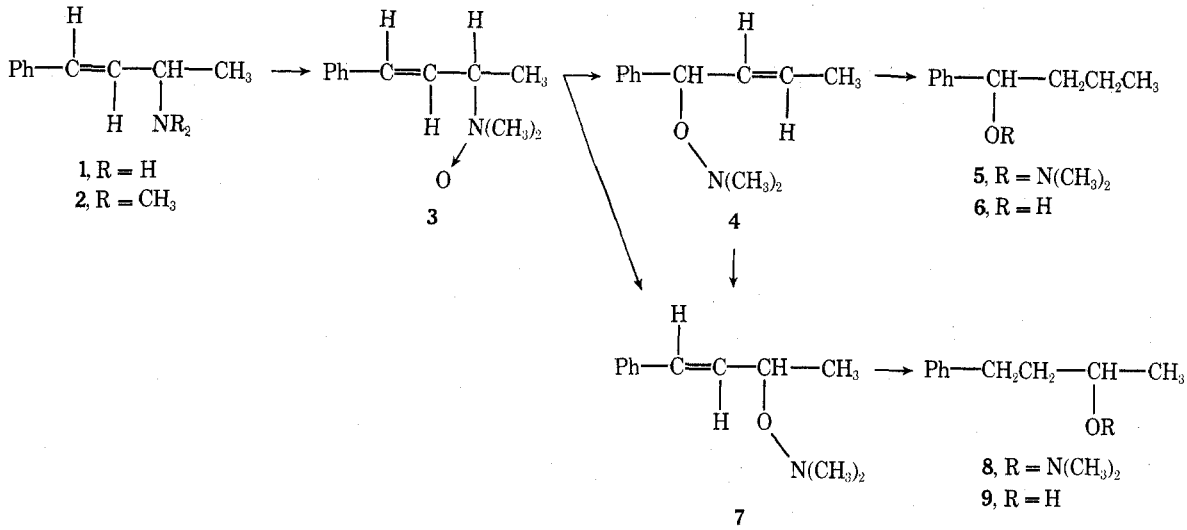
The [2,3]sigmatropic rearrangement of (*S*)-*N,N*-dimethyl-3-(*trans*-1-phenyl-1-butenyl)amine oxide to give (*S*)-*O*-*trans*-1-phenyl-2-butenyl-*N,N*-dimethylhydroxylamine was effected at −20° with nearly complete transfer of chirality from tetrahedral carbon to trigonal carbon. At higher temperature, the radical path prevailed to yield exclusively the [1,2] shift product, *O*-*trans*-1-methyl-3-phenyl-2-propenyl-*N,N*-dimethylhydroxylamine, with conservation of chirality to the extent of 20%.

In the preceding paper, we described the thermal [2,3]sigmatropic rearrangement of chiral amine oxide in which the chirality of nitrogen atom was nearly completely transferred to trigonal carbon at the expense of the former. We now wish to report another example of the same reaction in which the chirality of tetrahedral carbon was transferred to trigonal carbon.

The substrate used in the present study was the chiral amine oxide, (*S*)-*N,N*-dimethyl-3-(*trans*-1-phenyl-1-butenyl)amine oxide (**3**), prepared from (−)-*trans*-1-phenyl-3-amino-1-butene [(−)-**1**], $[\alpha]^{20}D$ −7.8°. The Eschweiler–Clarke methylation of (−)-**1**, followed by peracetic acid oxidation of the N-methylated amine (−)-**2**, $[\alpha]^{20}D$ −34.0°, afforded **3**, which was characterized by the picrate, $[\alpha]^{21}D$ −54.4°, in a parallel run starting from (−)-**2** having a rotation $[\alpha]^{18}D$ −36.4°. The *S* configuration[2] of (−)-**1** was established by chemical correlation of the enantiomeric (+)-**1** to (−)-benzoylalanine methyl ester of the well-defined *R* configuration,[3] through the consecutive N-benzoylation, barium permanganate cleavage, and esterification with diazomethane. The optical purity of (−)-**1** was determined to be 81% on the basis of the maximum rotation found by the optical resolution via (−)-malic acid salt.

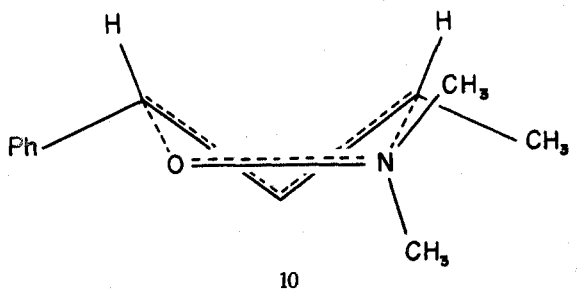
The amine oxide (**3**) thus obtained was allowed to stand at −20° for 24 days, during which **3** rearranged to *O*-*trans*-1-phenyl-2-butenyl-*N,N*-dimethylhydroxylamine (**4**) in 44% yield based on (−)-**2**. The trans geometry of the double bond in **4** was established by ir and ^1H NMR spectra in comparison with *trans*-1-phenyl-2-buten-1-ol. Since the rearrangement product **4** was not so stable as to permit one to observe constant rotation at room temperature, it was at once hydrogenated over platinum oxide to give (−)-*O*-1-phenylbutyl-*N,N*-dimethylhydroxylamine [(−)-**5**], $[\alpha]^{26}D$ −83.4°. Reductive N–O bond fission of (−)-**5** with zinc in



acetic acid afforded (−)-1-phenyl-1-butanol [(−)-**6**], $[\alpha]^{22}D$ −31.6°.

Successful transfer of the chirality originally residing on the tetrahedral carbon to the trigonal carbon was thus achieved in the present system. Since the *S* configuration of the end product (−)-**6** has been unambiguously established,[4] *the same configuration can be assigned to the parent* (−)-**5** and **4**. Consequently, the *S* configuration of the rearrangement product **4** was newly created at the expense of the *S* configuration of the substrate amine oxide (**3**). The optical purity of (−)-**6** proved to be 69% based on the reported maximum rotation $[\alpha]D$ −45.9°,[5] so that 85% optical activity was retained during the present process. It was reported that ca. 16% racemization occurred when the hydroxylamine derivative of (−)-benzyl alcohol-α-*d* was treated with zinc dust in acetic acid.[6] To assess the extent of racemization inherent to the method for N–O bond cleavage, (−)-1-phenyl-1-butanol[7] having a rotation $[\alpha]^{19}D$ −41.2° was subjected to exactly the same treatment and the recovered alcohol had a rotation of $[\alpha]^{20}D$ −35.4°, which corresponded to ca. 86% retention of optical activity. It then follows that the optical yield in the present self-immolative asymmetric synthesis can be looked upon as being nearly quantitative.

The complete transfer of chirality during the [2,3] shift supports the concerted mechanism and excludes the radical dissociation–recombination. There are two conceivable transition states expected for thermally allowed [2,3]sigmatropic rearrangement from the viewpoint of the conservation of orbital symmetry: doubly suprafacial and doubly antarafacial.[8] The finding that the (*S*)-*trans*-amine oxide (**3**) rearranged to give (*S*)-*trans*-hydroxylamine (**4**) cogently supports the fashion **10**. In this fashion, both fragments



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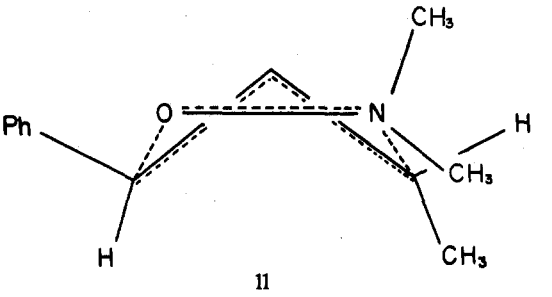
orient doubly suprafacial, which is geometrically preferred to the antarafacial modes. The preference of the mode **10** to an alternative suprafacial **11** could be rationalized by the unfavorable nonbonded interaction between methyl group and hydrogen atom which orient syn-quasi-axial in an envelope form of the latter.



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When the amine oxide (**3**) derived from (*R*)-(+)-**2**, $[\alpha]^{25}D$ 36.6° (87% optical purity), was heated in chloroform under reflux for 1 hr, the [1,2] shift product, (+)-*O*-*trans*-1-methyl-3-phenyl-2-propenyl-*N*,*N*-dimethylhydroxylamine [(+)-**7**], $[\alpha]^{25}D$ 6.9°, was obtained in an overall yield of 56% from **2** through **7**. There was no detectable contamination of the [2,3] shift product **4**.

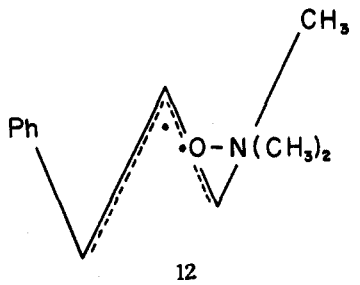
Hydrogenation of (+)-**7** over platinum oxide gave (−)-*O*-1-methyl-3-phenylpropyl-*N*,*N*-dimethylhydroxylamine (**8**), $[\alpha]^{25}D$ −6.6°. Subsequent treatment of (−)-**8** with zinc dust in acetic acid afforded (−)-1-phenyl-3-butanol (**9**), $[\alpha]^{26}D$ −3.2°. The *R* configuration can be safely assigned to (−)-**8** and (+)-**7**, and the optical purity was assessed to be 17% by transformation to (−)-**9** whose *R* configuration[9] and maximum rotation, $[\alpha]^{20}D$ −19.41°,[10] have been known.

The chirality at the carbon atom originally bonded to the nitrogen atom was conserved to the extent of 20% (corrected for the optical purity of the amine oxide used) at the same chiral center during the present thermal process.

An aliquot of the chloroform solution of the chiral amine oxide (**3**) was subjected to [2,3] rearrangement under the same condition described above and the resultant product **4** was then heated in chloroform under reflux for 1 hr. Along with a small amount of **4**, the compound (+)-**7** was obtained, which upon hydrogenation was converted into (−)-**8** having a rotation $[\alpha]^{27}D$ −6.5°. Consequently, the conservation of chirality in the course of the present consecutive [2,3] and [1,3] rearrangements compared well with that of the direct thermal [1,2] shift.

These facts show that the higher the temperature, the more the radical path prevails in competition with the [2,3] concerted process.[8] The [1,2] shift upon heating seems to take place via the classical Meisenheimer mechanism.[11] The radical dissociation–recombination is supported by the fact that the conservation of chirality at the carbon atom

was of the extent of 20%. The value is in accordance with the observation that the rearrangement of (+)-*N,N*-dimethylbenzyl-α-*d* amine oxide proceeded with 22–39% retention of configuration.[12] The radical pair intermediate can be formulated as explicit in **12**. *N,N*-Dimethylnitroxide



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radical is in juxtaposition to the allylic radical. The orientation seems to permit access of no less than 20% of retention at the chiral center concerned during the thermal process which has inevitable randomness.

It seems likely that the [1,3] shift from **4** to **7** involves a process of dissociation into two halves, since the magnitude of racemization is comparable with that of the direct [1,2] shift. The same solvent-caged radical pair was assumed in the [1,3] rearrangement of *O*-linalyl-*N,N*-dimethylhydroxylamine.[13] It can be explained by product stability that the [1,2] shift product was finally obtained on heating. The higher stability of **7** than **4** is rationalized by the conjugation of double bond with phenyl.

Experimental Section

(−)-*trans*-1-Phenyl-3-amino-1-butene [(−)-1]. The racemic amine[14] (30 g, 0.2 mol) was added to (+)-tartaric acid (30.6 g, 0.2 mol) in ethanol (1200 ml) and the salt formed was recrystallized twice from ethanol to yield colorless plates (11.4 g), mp 165–166°, $[\alpha]^{21}D$ 0.0° (*c* 0.20, ethanol). The amine liberated from the salt had bp 120–122° (20 mm), $n^{21}D$ 1.5614, $[\alpha]^{20}D$ −7.8° (*c* 10.0, benzene).

The optically pure (+) enantiomer was obtained via the (−)-malate salt, mp 157–158°, $[\alpha]^{26}D$ 35.1° (*c* 1.0, ethanol), $[\alpha]^{27}D$ 9.6° (*c* 9.8 benzene).

Configurational Correlation of (+)-1. The N-benzoylation of (+)-1 (4.0 g, 0.027 mol, $[\alpha]^{20}D$ 7.2°) was effected in the usual manner to give (+)-*trans*-1-phenyl-3-benzoylamino-1-butene (6.5 g, 95.2%), mp 132° (136–137° reported for the racemate[14]), $[\alpha]^{20}D$ 34.2° (*c* 1.0, methanol). The benzoylamine (2.5 g, 0.01 mol) was treated with barium permanganate in the reported manner[15] and the crude product was esterified by the standard method with diazomethane. Purification on a silica gel column with benzene–ethyl acetate (8:1) used as eluent and crystallization from ligroin yielded (−)-benzoylalanine methyl ester: mp 53–54° (lit.[3] 58°); $[\alpha]^{19}D$ −29° (*c* 2.0, acetylene tetrachloride); ir (KBr) ν_{NH} 3300, $\nu_{OC=O}$ 1745, $\nu_{NC=O}$ 1630 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.52 (d, 3 H, CH_3), 3.82 (s, 3 H, OCH_3), 4.62–5.13 (m, 1 H, CH), 6.65–7.08 (broad, 1 H, NH), 7.40–8.08 (m, 5 H, phenyl).

Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.75; H, 6.32; N, 6.76. Found: C, 63.75; H, 6.49; N, 6.94.

The ir and ^{1}H NMR spectra were identical in every respect with those of the authentic (*S*)-(+)-benzoylalanine methyl ester, which was derived from (*S*)-alanine, $[\alpha]^{19}D$ 33°.

(−)-*trans*-1-Phenyl-3-*N,N*-dimethylamino-1-butene [(−)-2]. The Eschweiler–Clarke methylation[16] of (−)-1 (4.0 g, 0.027 mol, $[\alpha]^{20}D$ −7.8°) with formic acid and formaldehyde gave (−)-**2** (2.3 g, 47.4%): bp 133–134° (21 mm); $n^{22}D$ 1.5351 [lit.[17] bp 139–140° (25 mm), $n^{25}D$ 1.5350 for the racemate]; $[\alpha]^{20}D$ −34.0° (*c* 10.0, benzene).

Picrate of *N,N*-Dimethyl-3-(*trans*-1-phenyl-1-butenyl)amine Oxide (3). Peracetic acid (40%, 1.3 g, 0.007 mol) was added dropwise at −40° to (−)-**2** (0.81 g, 0.0047 mol, $[\alpha]^{18}D$ −36.4°) in chloroform (20 ml). The reaction mixture was allowed to stand at −20° overnight and then made alkaline with 10% aqueous sodium hydroxide and the aqueous layer was extracted with chloroform (15 ml × 3). The combined extract was dried over anhydrous potassium carbonate and filtered. Picric acid (0.85 g, 0.0037 mol) in ethanol (20 ml) was added to the filtrate, and the mixture was stored in a refrigerator. The picrate salt deposited (0.75 g, 38.4%): mp 144–145°, $[\alpha]^{21}D$ −54.4° (*c* 0.50, methanol); ir (KBr) ν_{N-O}, $\delta_{=CH}$ (trans) 968, 962 cm^{-1}; ^{1}H NMR (Me_2SO-d_6) δ 1.57 (d, 3 H, CH_3), 3.30 (broad, 1 H, OH), 3.39 and 3.42 [s, 6 H, $N(CH_3)_2$], 4.50 (m, 1 H, CH), 6.15–7.08 (m, 2 H, CH=CH), 7.22–7.68 (m, 5 H, phenyl), 8.58 (s, 2 H, picrate).

Anal. Calcd for $C_{18}H_{20}N_4O_8$: C, 51.43; H, 4.80; N, 13.33. Found: C, 51.14; H, 4.98; N, 13.10.

[2,3] Rearrangement of 3. The amine oxide (**3**) was obtained by the oxidation of (−)-**2** (2.3 g, 0.013 mol, $[\alpha]^{20}D$ −34.0°) with 40% peracetic acid (3.8 g, 0.02 mol) in chloroform (60 ml) in exactly the same way as described above. The amine oxide extracted was allowed to stand still at −20° for 24 days. The chloroform solution was filtered through 50 g of activated alumina and evaporated in vacuo at 0°. *O-trans*-1-Phenyl-2-butenyl-*N,N*-dimethylhydroxylamine (**4**) was obtained in an overall yield of 44% from (−)-**2**: 1.1 g; ir (liquid) $\delta_{=CH}$ (trans) 962 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.70 (m, 3 H, CH_3), 2.47 [s, 6 H, $N(CH_3)_2$], 4.74–5.72 (m, 3 H, CH and CH=CH), 7.27 (m, 5 H, phenyl).

(−)-*O*-1-Phenylbutyl-*N,N*-dimethylhydroxylamine [(−)-5]. The hydrogenation of **4** (1.1 g) over platinum oxide in ethanol at 0° gave (−)-**5** (1.0 g, 90.1%). The analytical sample was obtained by preparative VPC (5% DEGS on Neosorb, 150°, He 80 ml/min): $n^{25}D$ 1.4842; $[\alpha]^{26}D$ −83.4° (*c* 6.0, benzene); ^{1}H NMR (CCl_4) δ 0.93 (m, 3 H, CH_3), 1.15–1.85 (m, 4 H, CH_2CH_2), 2.37 [s, 6 H, $N(CH_3)_2$], 4.43 (t, 1 H, CH), 7.19 (m, 5 H, phenyl).

(−)-1-Phenyl-1-butanol [(−)-6]. Zinc dust (2.0 g, 0.026 g-atom) and 30% acetic acid (20 ml) were added to (−)-**5** (1.0 g, 0.0052 mol, $[\alpha]^{26}D$ −83.4°). The mixture was heated under reflux for 5 hr and extracted with ether. The ether extract was washed with saturated sodium carbonate solution and water, dried over sodium sulfate, and evaporated. (−)-1-Phenyl-1-butanol [(−)-**6**] was obtained (0.58 g, 74.6%). The analytical sample was obtained by preparative VPC (5% PEG 20M on Neosorb, 200°, He 70 ml/min): mp 36–37° (lit.[5] 49–50° for pure enantiomer), $[\alpha]^{22}D$ −31.6° (*c* 10.0, benzene); ^{1}H NMR ($CDCl_3$) δ 0.98 (m, 3 H, CH_3), 1.14–1.95 (m, 4 H, CH_2CH_2), 2.03 (s, 1 H, OH), 4.73 (t, 1 H, CH), 7.42 (m, 5 H, phenyl).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.77; H, 9.53.

Zinc dust (4.0 g) and 30% acetic acid (40 ml) were added to (−)-**6** (1.55 g, $[\alpha]^{19}D$ −41.2°) and the mixture was treated in exactly the same way as described above. The recovered alcohol (−)-**6** (1.3 g) had $[\alpha]^{20}D$ −35.4°.

[1,2] Rearrangement of 3 to Give (+)-*O-trans*-1-Methyl-3-phenyl-2-propenyl-*N,N*-dimethylhydroxylamine [(+)-7]. The amine oxide **3**, obtained from (+)-**2** (5.0 g, $[\alpha]^{25}D$ 36.6°) and 40% peracetic acid (8.2 g) in chloroform (120 ml), was divided into two portions, (1) 200 ml and (2) 160 ml.

The portion 1 was heated under reflux for 1 hr and the product was purified on an alumina column with *n*-hexane used as eluent. (+)-**7** (1.7 g, 56.2%): $n^{26}D$ 1.5178; $[\alpha]^{25}D$ 6.9° (c 5.8, benzene); ir (liquid) $\delta_{=CH}$ (trans) 955 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.27 (d, 3 H, CH_3), 2.55 [s, 6 H, $N(CH_3)_2$], 4.35 (m, 1 H, CH), 6.00–6.78 (m, 2 H, CH=CH), 7.20–7.62 (m, 5 H, phenyl).

(−)-*O*-1-Methyl-3-phenylpropyl-*N,N*-dimethylhydroxylamine [(−)-8]. The hydrogenation of (+)-**7** (1.7 g, $[\alpha]^{25}D$ 6.9°) over platinum oxide in ethanol gave (−)-**8** (1.3 g, 75.8%). The analytical sample was obtained by preparative VPC (5% PEG 20M on Neosorb, 180°, He 80 ml/min): $n^{26}D$ 1.4823; $[\alpha]^{25}D$ −6.6° (*c* 10.3, benzene); ^{1}H NMR (CCl_4) δ 1.15 (d, 3 H, CH_3), 1.34–2.17 and 2.58–2.99 (m, 4 H, CH_2CH_2), 2.53 [s, 6 H, $N(CH_3)_2$], 3.71 (m, 1 H, CH), 7.27 (m, 5 H, phenyl).

(−)-1-Phenyl-3-butanol [(−)-9]. The zinc dust–acetic acid treatment of (−)-**8** (0.8 g, $[\alpha]^{25}D$ −6.6°) and the subsequent work-up in exactly the same manner as described for (−)-**6** yielded (−)-**9** (0.64 g, 96.4%): $n^{28}D$ 1.5090; $[\alpha]^{26}D$ −3.2° (*c* 6.2, benzene); ^{1}H NMR (CCl_4) δ 1.17 (d, 3 H, CH_3), 1.49–1.92 and 2.53–2.90 (m, 4 H, CH_2CH_2), 2.13 (s, 1 H, OH), 3.75 (m, 1 H, CH), 7.19 (m, 5 H, phenyl); phenylurethane, mp 113–114° (lit.[18] mp 113° for the racemate).

Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 76.03; H, 7.27; N, 5.25.

Consecutive [2,3] and [1,3] Rearrangements of 3. The portion 2 containing the amine oxide **3** was first allowed to stand at −20° and worked up in the same way as described for **4** to afford the same product **4** (1.2 g, 48%), which was then heated in chloroform under reflux for 1 hr to yield crude (+)-**7** (1.1 g, 91.6%). The contamination by **4** was detected to an extent of ca. 17% as estimated by ^{1}H NMR spectroscopy. The product **7** was hydrogenated

to give (−)-8, which on purification by preparative VPC afforded the analytical sample, $[\alpha]^{27}D$ −6.5°.

trans-1-Phenyl-2-buten-1-ol:[19] ir (liquid) $\delta_{=CH}$ (trans) 958 cm^{-1}; ^1H NMR (CCl_4) δ 1.72 (m, 3 H, CH_3), 2.56 (s, 1 H, OH), 4.94–5.84 (m, 3 H, CH and CH=CH), 7.34 (m, 5 H, phenyl).

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Registry No.—(−)-1, 57128-66-2; (−)-1 tartrate, 57128-67-3; (+)-1, 51773-65-0; (+)-1 malate, 57066-04-3; (±)-1, 57128-68-4; (−)-2, 57066-05-4; 3 picrate, 57066-07-6; 4, 51729-87-4; (−)-5, 51729-88-5; (−)-6, 22135-49-5; (+)-7, 57066-08-7; (−)-8, 57066-09-8; (−)-9, 39516-03-5; (−)-9 phenylurethane, 57066-10-1; (+)-*trans*-1-phenyl-3-benzoylamino-1-butene, 57066-11-2; (−)-benzoylalanine methyl ester, 7260-27-7; *trans*-1-phenyl-2-buten-1-ol, 52755-39-2.

References and Notes

(1) A preliminary communication on this subject appeared: Y. Yamamoto, J. Oda, and Y. Inouye, *J. Chem. Soc., Chem. Commun.*, 848 (1973).
(2) In the preliminary communication,[1] we erroneously deduced the *R* configuration to (−)-1 based on the catalytic hydrogenation of (−)-1 to give (+)-1-phenyl-3-aminobutane, to which the *R* configuration was inferred by Červinka.[9] In contrast, the opposite *S* configuration was claimed for the same (+) enantiomer by Terent'ev [*Zh. Obshch. Khim.*, **35**, 1538 (1965); *Chem. Abstr.*, **63**, 17854*h* (1965)]. We were inextricably confused by this situation and so we worked out the absolute assignment of configuration by independent and unambiguous means in the present study.
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Adenine Nucleosides Derived from 6-Deoxyhexofuranoses[1]

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Methyl 2,3-*O*-isopropylidene-β-L-gulofuranoside (**2**) was converted into methyl 2,3-*O*-isopropylidene-5,6-di-*O*-methanesulfonyl-β-L-gulofuranoside (**3**) and treatment of this with lithium aluminum hydride afforded methyl 6-deoxy-2,3-*O*-isopropylidene-β-L-gulofuranoside (**4**). The 5-*O*-benzoate (**5**) was prepared and subjected to acetolysis under conditions known to result in epimerization at C-2. The acetolysis product was condensed with 6-benzamidochloromercuripurine by the titanium tetrachloride method. Removal of blocking groups afforded 9-(6-deoxy-α-L-idofuranosyl)adenine (**8**). Methyl 5-*O*-benzoyl-6-deoxy-2,3-*O*-isopropylidene-β-D-gulofuranoside (**9**) was used to prepare 9-(6-deoxy-β-D-gulofuranosyl)adenine (**14**). First, the isopropylidene group was removed and replaced with benzoates. Then the methoxyl group was exchanged for an acetoxyl group and **14** was prepared by the titanium tetrachloride coupling method. 9-(6-Deoxy-β-L-gulofuranosyl)adenine (**15**) was prepared starting from **5** by a series of reactions which were identical with the preparation of **14**. 9-(6-Deoxy-α-D-idofuranosyl)adenine (**16**) was prepared by acetolysis of **9** and coupling to the base as described for **8**. Nucleoside **8** was a substrate for adenosine deaminase from calf intestinal mucosa.

Nucleosides derived from 6-deoxyhexofuranoses are of potential use in this laboratory as precursors for the synthesis of other compounds of biological interest. However, some of these nucleosides may be of biological value in their own right. For instance, it has been demonstrated that 9-(6-deoxy-β-D-allofuranosyl)adenine is an inhibitor of adenine phosphoribosyl transferase (EC 2.4.2.7),[2] an important enzyme in nucleic acid metabolism. Furthermore, this compound is capable of acting as a substrate for adenosine deaminase (adenosine aminohydrolase, EC 3.5.4.4) and this is also the case for the 5′ epimer, 9-(6-deoxy-α-L-talofuranosyl)adenine.[3] These findings indicate that such compounds do have the ability to bind to enzymes of nucleic acid metabolism and may be useful antimetabolites.

A series of 6-deoxyhexofuranosyl nucleosides was originally prepared by Baker and co-workers. They reported the synthesis of adenine nucleosides derived from 6 deoxy-L-mannose,[4a] 6-deoxy-D-allose,[4b] 6-deoxy-D-glucose,[4c] 6-deoxy-L-idose,[4d] and 6-deoxy-L-talose.[4e] It has recently been shown that the compound reported in ref 4a as 9-(6-deoxy-α-L-mannofuranosyl)adenine was incorrect and the real nucleoside bearing this name was prepared and completely structure proofed.[5] It was also shown by Ryan et al.[6] that the nucleoside reported to be 9-(6-deoxy-α-L-idofuranosyl)adenine was really 9-(5-deoxy-β-D-*xylo*-hexofuranosyl)adenine on the basis of the NMR spectrum which lacked a peak for a terminal methyl group. Later work[7] verified that treatment of 6-*O*-benzoyl-2,3-*O*-isopropylidene-5-*O*-*p*-toluenesulfonyl-α-D-glucofuranose with lithium aluminum hydride yielded 5-deoxy-1,2-*O*-isopropylidene-β-D-*xylo*-hexofuranose rather than 6-deoxy-1,2-*O*-isopropylidene-α-L-idofuranose as assumed by Baker and co-workers[4d] when they prepared it as a starting material. Since there appears to be no report in the literature dealing with the synthesis of 9-(6-deoxy-α-L-idofuranosyl)adenine, it is probable that biological data reported[8] under this name are actually for the 5′-deoxy analogue instead. The original intent of the present work was the preparation of 9-(6-deoxy-β-D-gulofuranosyl)adenine, a heretofore unknown nucleoside analogue. Owing to the recent development of some rather convenient synthetic procedures, this work has been extended to include the preparation of both enantiomers of adenine nucleosides derived from 6-deoxygulose and 6-deoxyidose.