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Self-Immolative Asymmetric Synthesis. I. Allylic Rearrangement of Optically Active Amine Oxide[1]

Minoru Moriwaki,[2] Yukio Yamamoto, Jun'ichi Oda, and Yuzo Inouye*

Institute for Chemical Research, Kyoto University, Uji, Kyoto, Japan

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Transfer of chirality from tetracoordinate nitrogen to trigonal carbon was achieved in the allylic rearrangement of (*R*)-(+)-*N*-*trans*-crotyl-*N*-methyl-*p*-toluidine oxide to (*S*)-(+)-*O*-methylvinylcarbinyl-*p*-tolylhydroxylamine with nearly complete conservation of chirality. The present thermally allowed [2,3]sigmatropic rearrangement proceeds via a transition state conformation such as to meet the orbital symmetry requirements in a doubly suprafacial fashion.

Extensive studies on [2,3]sigmatropic rearrangements have been made during the last few years and the accumulated knowledge[3] suggests that this process proceeds through a five-membered cyclic transition state of a doubly suprafacial migration. The transition state is of the Hückel type, and since six electrons participate, the reaction is expected to be thermally allowed in accordance with the Woodward–Hoffmann orbital symmetry rule.[4]

The [2,3] shifts are the anionic equivalent of the Cope rearrangement, and like the [3,3] changes, are not confined to carbon systems,[5] but also involve many hetero systems. The Wittig,[6] Stevens,[7] and Meisenheimer rearrangements of allylic systems,[8] the Sommelet rearrangement,[9] the rearrangements of allylic sulfonium ylides,[10] sulfenates,[11] phosphinates,[12] amidoammonium salts[13] and other hetero systems[14] can be categorized as [2,3]sigmatropic processes.

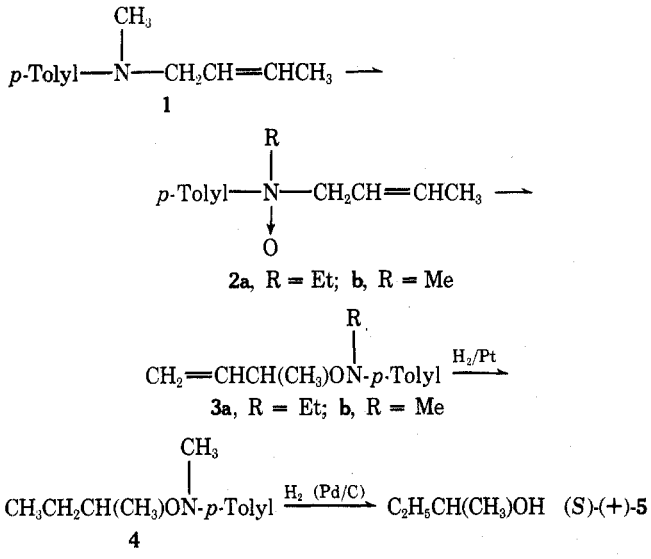
It is also known that this process is accompanied by a second pathway of higher activation energy, shown to be a radical-pair mechanism. The mechanistic difference depends on molecular environment and reaction conditions. In cases where the substrate has an allylic group, the concerted [2,3] shift competes favorably with the radical process. The former usually has the lower activation energy, as revealed by the fact that the proportion of the product which is formed by the concerted pathway increases at lower temperature. In contrast, the rearrangement of nonallylic compounds proceeds through a radical dissociation–recombination as demonstrated in the Wittig rearrangement of nonallylic ethers[15] and in the rearrangement of benzylamine oxide.[16]

In a preliminary report,[1] we described the first example of self-immolative asymmetric synthesis, in which the chirality on tetracoordinate nitrogen atom of (+)-*N*-*trans*-crotyl-*N*-ethyl-*p*-toluidine oxide (**2a**) was transferred, upon heating, completely to the trigonal carbon to give (+)-*O*-methylvinylcarbinyl-*N*-ethyl-*p*-tolylhydroxylamine (**3a**). However, since neither the absolute configuration nor the maximum rotation of **2a** was heretofore known, it was impossible to assess the degree of stereoselectivity and to formulate the transition state topology with certainty.

We now present unambiguous stereochemical evidence supporting the concerted nature of the [2,3]sigmatropic rearrangements of allylic amine oxide.

(*R*)-(+)-*N*-*trans*-Crotyl-*N*-methyl-*p*-toluidine oxide[17] (**2b**) was derived from the parent amine (**1**) by oxidation with *O,O*-dibenzoyl-L-pertartaric acid in chilled chloroform. Reflux of (+)-**2b** in 10% aqueous sodium hydroxide for 30 min gave (+)-*O*-methylvinylcarbinyl-*N*-methyl-*p*-tolylhydroxylamine (**3b**, $[\alpha]_D$ 2.42°) in 90% yield. This shows that a sigmatropic [2,3] allylic shift took place in the present system, as was the case with the *N*-ethyl homologue.[1] The absolute configuration of the newly created tetrahedral carbon was correlated by the sequential reduction to (*S*)-2-butanol (**5**) (Scheme I). Catalytic hydrogenation of (+)-**3b** over platinum oxide yielded (+)-*O*-2-butyl-*N*-methyl-*p*-tolylhydroxylamine (**4**, $[\alpha]_D$ 2.38°). Hydrogenol-

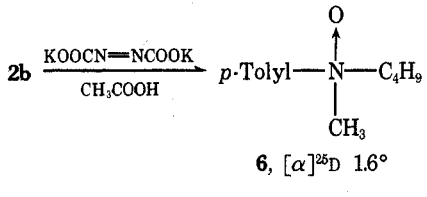
Scheme I



ysis of (+)-4 over palladium on charcoal yielded 2-butanol (**5**, $[\alpha]$D 1.71°), together with *N*-methyl-*p*-toluidine. Since the *S* configuration of (+)-**5** has been unequivocally established,[18] the same configuration can be assigned to (+)-**3b** and (+)-**4**, and their optical purity was 13.6% based on the maximum rotation, 13°,[14] of the end product (**5**).

The absolute assignment of the nitrogen chirality as well as the enantiomeric purity of the starting amine oxide (+)-**2b**, crucial to the mechanistic picture for the present rearrangement, were obtained with success by the Pirkle method[20] of magnetic nonequivalence of chemical shifts in the ^{1}H NMR spectrum. To simplify the correlations based on Pirkle's chiral solute–chiral solvent interaction model, the double bond was first reduced so that the aromatic ring is the only remaining unsaturated substituent. Therefore, (+)-**2b** was reduced by the use of potassium diazocarbonate to (+)-**6**, $[\alpha]$D 1.65°, without disturbing the chiral nitrogen center (Scheme II). For more reliable determination of en-

Scheme II



antiomeric purity and sense of nonequivalence, we prepared (+)-**6** of a higher rotation, $[\alpha]$D 6.7°, according to the literature method.

With this optically active sample, the determination of absolute configuration and enantiomeric purity was undertaken. In optically active (*S*)-(+)-2,2,2-trifluoro(α-naphthyl)ethanol[21] (**7**), the *N*-methyl of (+)-enriched *N*-methyl-*N*-*n*-butyl-*p*-toluidine oxide shows a high field sense of nonequivalence (17 Hz), whereas in the enantiomeric (*R*)-(−) alcohol **7**, *N*-methyl shows a low field sense of nonequivalence (220 MHz at 29°) (Figures 1 and 2). Using Pirkle's solvation model,[20] one concludes that the methyl resonance should appear at higher field in the *R*–*S* solvate than in the *R*–*R*, while the opposite should be true for the *n*-butyl resonance. However, the latter resonance are coincident.

Based on the separation pattern and peak heights of the *N*-methyl resonances, it is concluded that (+)-amine oxide

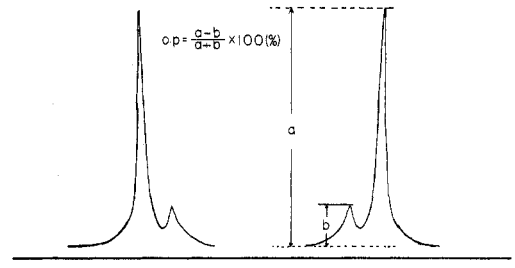


Figure 1. Enantiomeric nonequivalence exhibited by (+) enriched *N*-Methyl-*N*-*n*-butyl-*p*-toluidine oxide in optically active (*S*)-(+)- or (*R*)-(−)-2,2,2-trifluoro(α-naphthyl)ethanol at 220 MHz and 29°.

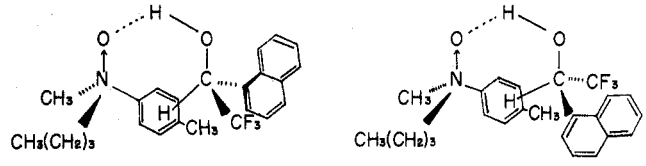


Figure 2. Conformations of the solvate between (*R*)-(+) *N*-oxide and (*S*)-(+) or (*R*)-(−) alcohol.

6 possesses the *R* configuration and the enantiomeric purity is 64.5%; therefore, the maximum rotation of the enantiomerically pure material is 10.4°. It then follows that the parent (+)-*N*-*trans*-crotyl-*N*-methyl-*p*-toluidine oxide (+)-(**2b**) has the same *R* configuration and an enantiomeric purity of 16%.

Independent confirmation of the enantiomeric purity was provided also by observation of the ^{1}H NMR spectrum of (+)-**6**, $[\alpha]$D 5.7°, in the presence of tris[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]europium.[22] The separation of enantiotopic methyl singlets was 22 Hz. The peak height determination shows the enantiomeric excess to be 57.3% and then the maximum rotation to be 10°, in good agreement with that by the Pirkle method.

Consequently, the conservation of enantiomeric purity during the rearrangement was as high as 83% and may well be looked upon as being nearly complete when one takes into consideration the subsequent chemical transformations to 2-butanol **5**. Thus, the chirality of the tetracoordinate nitrogen atom in (+)-**2b** was transferred to the originally nondissymmetric trigonal carbon, giving rise to a newly created asymmetric carbon at the expense of nitrogen chirality.

With the knowledge of the *R* configuration of the starting amine oxide (+)-**2b** and the *S* configuration of the rearrangement product (+)-**4**, combined with the nearly complete conservation of chirality during the process, it can be concluded that the present rearrangement proceeds through a five-membered cyclic transition state by a concerted mechanism and the radical dissociation–recombination mechanism can be excluded. Concerning the potential generality to the stereochemistry of [2,3]sigmatropic rearrangement, Baldwin[3] stated that a doubly suprafacial transition state is more favored than a doubly antarafacial mode because of the geometrical and therefore energetic stringency of the latter. Application of the concept enables us to formulate the transition state topology for the present system. Figure 3 depicts such two rotational fashions of suprafacial modes **8** and **9**. The stereochemical evidence presented above cogently supports the mode **8** as the preferred one. Consistently, the nonbonded interaction between methyl and *N*-*p*-tolyl groups is minimized in **8**, which is therefore thermodynamically more favored.

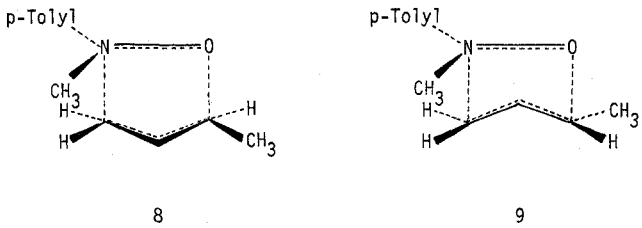


Figure 3.

By analogy, the discussion may hold also for the thermal rearrangement of the *N*-ethyl homologue reported in the preliminary communication.[1]

Experimental Section

Melting and boiling points are uncorrected. Ir spectra were recorded on a Hitachi EPS-2 and ^{1}H NMR spectra on a Varian A-60 spectrometer. Optical rotations were observed with a Yanagimoto ORD-185A recording spectrophotometer.

***N-trans*-Crotyl-*N*-methyl-*p*-toluidine (1).** Crotyl bromide (15 g, 0.11 mol) in benzene (30 ml) was slowly added with stirring to *N*-methyl-*p*-toluidine[23] (10 g, 0.083 mol) in benzene (30 ml). The reaction mixture was heated for 30 min with stirring. After adding 10% aqueous sodium hydroxide (50 ml), the product was extracted with ether (200 ml), washed successively with dilute hydrochloric acid, dilute aqueous sodium hydroxide, and water, and dried over sodium sulfate. *N-trans*-Crotyl-*N*-methyl-*p*-toluidine distilled at 107–110° (8 mm); n^{28}D 1.5343; 11.5 g (79.3%); ir (liquid) $\nu_{C=C}$ (trans) 1670, δ_{CH} (trans) 970 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.68 (m, 3 H, crotyl CH_3), 2.25 (s, 3 H, ring CH_3), 2.84 (s, 3 H, NCH_3), 3.70 (m, 2 H, NCH_2), 5.68–5.18 (m, 2 H, CH=CH), 7.18–6.50 (m, 4 H, phenyl protons).

***N*-Methyl-*N*-*n*-butyl-*p*-toluidine.** *n*-Butyl bromide (30 g, 0.22 mol) was added to *N*-methyl-*p*-toluidine (24 g, 0.2 mol) in benzene (50 ml). The mixture was refluxed for 3 days. After adding 15% aqueous sodium hydroxide (70 ml), the product was extracted with ether, washed with dilute hydrochloric acid, dilute aqueous sodium hydroxide, and water, and dried over sodium carbonate. Distillation gave *N*-methyl-*N*-*n*-butyl-*p*-toluidine: bp 105–107° (8 mm); n^{25}D 1.5210; 25.1 g (95.1%); ^{1}H NMR ($CDCl_3$) δ 0.90 (t, 3 H, butyl CH_3), 1.41 (m, 4 H, $NCH_2CH_2CH_2$), 2.20 (s, 3 H, ring CH_3), 2.84 (s, 3 H, NCH_3), 3.22 (m, 2 H, NCH_2), 7.17–6.45 (m, 4 H, phenyl protons).

***(R)*-(+)-*N*-Methyl-*N*-*n*-butyl-*p*-toluidine Oxide (6).** *N*-Methyl-*N*-*n*-butyl-*p*-toluidine (10 g, 0.057 mol) was allowed to react with 1 equiv of 40% peracetic acid in chilled chloroform with stirring and the reaction mixture was stirred for a further 5 days at room temperature. After adding 10% aqueous sodium hydroxide under cooling, *N*-methyl-*N*-*n*-butyl-*p*-toluidine oxide was extracted with three 40-ml portions of chloroform. The combined chloroform extracts were washed with 10% aqueous sodium hydroxide, dried over potassium carbonate, and evaporated under reduced pressure to give crude *N*-methyl-*N*-*n*-butyl-*p*-toluidine oxide (10.2 g, 91.7%).

(−)-*O,O*-Dibenzoyltartaric acid[24] (18 g, 0.057 mol) in ethanol (20 ml) was added with stirring to the crude amine oxide (10 g) in ethanol (30 ml). After standing still in the refrigerator overnight, crude precipitate [$[\alpha]^{25}$D −67.7° (*c* 0.3), 15 g, 50%] was collected. Several recrystallizations from ethanol (99.5%) gave the tartrate salt with constant physical properties: mp 158°; $[\alpha]^{25}$D −76.3° (*c* 0.82, MeOH); 4.2 g (13.4%); ir (KBr) ν_{OH} 3500, $\nu_{C=O}$ 1725 cm^{-1}.

Anal. Calcd for $C_{30}H_{33}NO_9$: C, 65.32; H, 6.03; N, 2.54. Found: C, 65.28; H, 6.18; N, 2.54.

The optically active amine oxide liberated from the salt was identified by comparison of ir and ^{1}H NMR spectra with those of an authentic sample: $[\alpha]^{25}$D +6.7° (*c* 3.57, chloroform); ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 3 H, butyl CH_3), 1.70–0.95 (m, 4 H, $NCH_2CH_2CH_2$), 2.40 (s, 3 H, ring CH_3), 3.50 (s, 3 H, NCH_3), 3.60 (m, 2 H, NCH_2), 7.83–7.12 (m, 4 H, phenyl protons).

(+)-*N-trans*-Crotyl-*N*-methyl-*p*-toluidine Oxide (2b). *N-trans*-Crotyl-*N*-methyl-*p*-toluidine (1, 15 g, 0.078 mol) was oxidized at −70 to −75° with an equivalent amount of (*R,R*)-*O,O*-dibenzoylpertartaric acid in chloroform for 1 hr. The reaction mixture was kept at −20° overnight and then the solvent was evaporated at −10° under reduced pressure. Absolute ethanol (40 ml) was added to the residue and the solution was allowed to stand still in a refrigerator. The crystalline deposite (9.3 g) was recrystallized two times from warm ethanol. *N-trans*-Crotyl-*N*-methyl-*p*-toluidine oxide dibenzoyltartrate had mp 137–140.5° dec; $[\alpha]^{25}$D −78.4° (*c* 1.20, MeOH).

Anal. Calcd for $C_{30}H_{31}NO_9$: C, 65.56; H, 5.69; N, 2.55. Found: C, 65.26; H, 5.70; N, 2.53.

Picrate. The dibenzoyltartrate salt ($[\alpha]^{20}$D −75°) was decomposed with 10% aqueous sodium hydroxide below −10°. The aqueous mixture was extracted with cold chloroform and the chloroform layer was washed with dilute aqueous sodium hydroxide and dried over potassium carbonate. After removal of solvent under reduced pressure below −15°, an alcohol solution of picric acid was added slowly to the oily residue and the solution was kept cold in a refrigerator for at least 3 days: yellow needles, mp 118–120° dec, $[\alpha]^{18}$D 0°; $[\alpha]^{18}_{546}$ ±1°; $[\alpha]^{18}_{436}$ 19° (*c* 1.43, MeOH).

Anal. Calcd for $C_{18}H_{20}N_4O_8$: C, 51.15; H, 5.01; N, 13.23. Found: C, 51.42; H, 4.80; N, 13.33.

Reduction of *N-trans*-Crotyl-*N*-methyl-*p*-toluidine Oxide Dibenzoyltartrate with Potassium Diazocarbonate. Potassium diazocarbonate (900 mg) in methanol was added to the (−)-dibenzoyltartrate salt (500 mg) in methanol (6 ml), and acetic acid (500 mg) in methanol (3 ml) was slowly added to the mixture at 4° in a nitrogen atmosphere. The reaction mixture was stirred at 4° for 24 hr and was filtered, made alkaline, and extracted with three 10-ml portions of chloroform. The combined extracts were washed with 10% aqueous sodium hydroxide, dried over potassium carbonate, and evaporated under reduced pressure. The residue was separated on an alumina column. Elution with chloroform afforded first the rearrangement product (3b), and then with chloroform–methanol (3:1), the reduction product, *N*-methyl-*N*-*n*-butyl-*p*-toluidine oxide (6). The ir and ^{1}H NMR spectra were identical in every respect with those of the authentic sample: 32 mg (17.8%); $[\alpha]^{25}$D 1.6° (*c* 6.50, chloroform).

Rearrangement of Optically Active *N-trans*-Crotyl-*N*-methyl-*p*-toluidine Oxide (2b). The benzoyltartrate salt of *N-trans*-crotyl-*N*-methyl-*p*-toluidine oxide ($[\alpha]^{25}$D −78.4°, mp 137–140.5°, 8 g) was decomposed in 10% aqueous sodium hydroxide, and the liberated amine oxide was extracted with two 50-ml portions of chloroform. The combined chloroform extracts were evaporated, and the residue was heated in an alkaline solution for 1 hr. After cooling, the product was extracted with ether (200 ml), washed with dilute hydrochloric acid, dilute sodium hydroxide, and water, and then dried over sodium sulfate. Distillation gave (+)-*O*-2-butenyl-*N*-methyl-*p*-tolylhydroxylamine (3b): 2.5 g (89.3%); bp 95–98° (4 mm); n^{22}D 1.5180; $[\alpha]^{20}$D 2.42° (*c* 1.25, chloroform); ir (liquid) $\nu_{C=CH_2}$ 1640 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.30 (d, 3 H, $CHCH_3$), 2.30 (s, 3 H, ring CH_3), 3.00 (s, 3 H, NCH_3), 4.32 (m, 1 H, $CHCH_3$), 6.40–4.90 (m, 3 H, $CH=CH_2$), 7.10–6.80 (s, 4 H, phenyl protons).

Hydrogenation of (+)-*O*-2-Butenyl-*N*-methyl-*p*-tolylhydroxylamine (3b). (+)-*O*-2-Butenyl-*N*-methyl-*p*-tolylhydroxylamine (3b, 2.5 g, 0.013 mol, $[\alpha]^{20}$D 2.42°) was hydrogenated over a catalytic amount of platinum oxide in ether (150 ml). An equivalent amount of hydrogen was absorbed (250 ml) at room temperature. The catalyst was filtered off and the filtrate was washed with dilute hydrochloric acid, dilute aqueous sodium hydroxide, and water and dried over sodium sulfate. (+)-*O*-2-Butyl-*N*-methyl-*p*-tolylhydroxylamine (4) distilled at 80–82° (3 mm): n^{22}D 1.4997; $[\alpha]^{20}$D 2.38° (*c* 1.82, chloroform); 2.4 g (96%); ^{1}H NMR ($CDCl_3$) δ 0.92 (t, 3 H, CH_2CH_3), 1.20 (d, 3 H, $CHCH_3$), 2.00 (m, 2 H, CH_2CH_3), 2.30 (s, 3 H, ring CH_3), 3.00 (s, 3 H, NCH_3), 3.74 (m, 1 H, $CHCH_3$), 7.10–6.80 (s, 4 H, phenyl protons).

Hydrogenolysis of (+)-*O*-2-Butyl-*N*-methyl-*p*-tolylhydroxylamine (4). The hydroxylamine (+)-4 ($[\alpha]^{23}$D 2.38°, 2.1 g, 0.011 mol) was hydrogenolized in ether (30 ml) containing 500 mg of palladinized carbon. Hydrogenolysis proceeded very slowly at room temperature until 60% of the theoretical amount of hydrogen was absorbed, and did not proceed any further. After filtration, the solvent was removed below 50° and the residue was carefully distilled to give (*S*)-(+)-2-butanol boiling at 100–102°, n^{18}D 1.3985, $[\alpha]^{20}$D 1.71° (*c* 1.46, EtOH), optical purity 13.2% based on the reported maximum rotation ±13°. The ir and ^{1}H NMR spectra and other physical properties except optical rotation were identical with those of the authentic sample.

Acknowledgment. The authors are indebted to Professor W. H. Pirkle of the University of Illinois for his helpful advice.

Registry No.—1, 57049-22-6; 2b, 57049-23-7; 2b dibenzoyltartrate salt, 57049-24-8; 2b picrate, 57049-25-9; 3b, 57049-26-0; 4, 57049-27-1; 6, 57049-28-2; 6 dibenzoyltartrate salt, 57049-29-3;

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]

Yukio Yamamoto, Jun'ichi Oda, and Yuzo Inouye*

Institute for Chemical Research, Kyoto University, Uji, Kyoto, Japan

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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