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Rearrangement of Indene Skeletons under Mild Conditions

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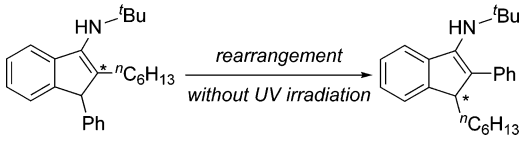

Isomerization between two isomers of 1,2-disubstituted 3-aminoindenes occurs via the rearrangement of indene frameworks. In contrast to previous rearrangements of indene derivatives, which occur under high-temperature conditions or the irradiation of light, this rearrangement proceeds at room temperature without UV light irradiation. An amino group at the 3-position plays an important role to accelerate the rearrangement under mild conditions.

Introduction

Rearrangement of carbon frameworks is one of the fundamental reactions in organic chemistry. Some well-known examples utilizing rearrangement include the pinacol−pinacolone rearrangement,[1] Wagner−Meerwein rearrangement,[2] Beckmann rearrangement,[3] Cope rearrangement,[4] rearrangement of vinylcyclopropane,[5] rearrangement of di-π-methane,[6] and photochemical or transition-metal-promoted isomerization of cyclopropenes and cyclopentadienes under UV irradiation.[7] Some examples of the isomerization of indene derivatives have also been reported, although the reaction needs harsh conditions[8] or irradiation of UV light.[9] We report herein on a rearrangement of aminoindene derivatives that proceeds even at room temperature without UV irradiation. Investigations on the isomerization mechanism of the aminoindene derivatives are also described.

Results and Discussion

We have already reported on a rhenium complex ([ReBr(CO)$_3$(thf)]$_2$) catalyzed synthesis of aminoindene derivatives by the reactions of aromatic aldimines with internal acetylenes.[10] In the case of using dissymmetric acetylenes, two aminoindene isomers were obtained (eq 1). In this reaction, the ratio of the

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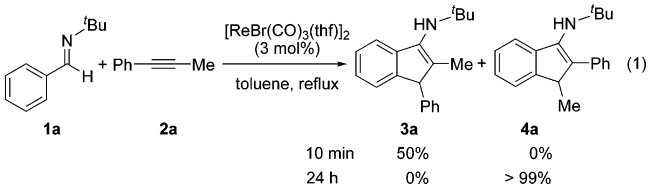
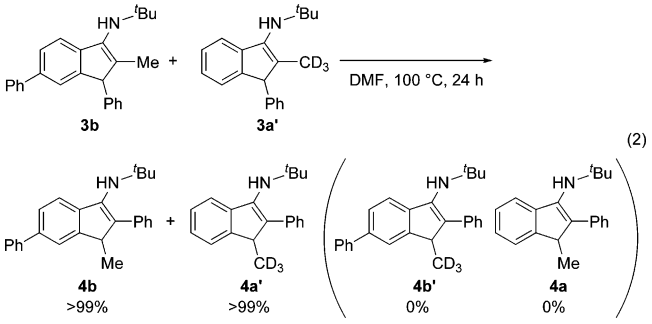


two aminoindene derivatives was reversed as the reaction time increased (eq 1). For example, the treatment of aromatic aldimine **1a** with 1-phenyl-1-propyne (**2a**) in toluene under reflux conditions for 10 min gave only aminoindene derivative **3a** in 50% yield. In contrast, after 24 h, **3a** disappeared and only aminoindene derivative **4a** was obtained quantitatively. These results indicate that **3a** was isomerized to **4a** under the reaction conditions. In fact, by refluxing the solution of the isolated aminoindene derivative **3a** in the absence of the rhenium complex $[ReBr(CO)_3(thf)]_2$ in toluene for 24 h, aminoindene isomer **4a** was formed in 35% yield and **3a** was recovered in 65% yield.[11]

We examined the solvent effect on the isomerization rates of aminoindene derivative **3a** (Table 1). In toluene, the rate of isomerization from **3a** to **4a** was slow (Table 1, entry 1). The rate of isomerization increased slightly with rather polar solvents, such as tetrahydrofuran and 1,2-dichloroethane (Table 1, entries 2 and 3). When *N*,*N*-dimethylformamide (DMF), acetonitrile, or DMSO was used as the solvent, the rate of isomerization increased substantially (Table 1, entries 4−6). The results show that the rate of isomerization of aminoindene derivative **3a** to **4a** becomes faster with polar solvents, and thus the isomerization proceeds via a polar intermediate.

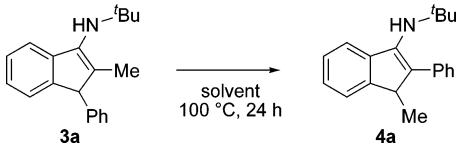
The next question is whether the isomerization proceeds via an intra- or intermolecular reaction. The isomerization reaction of aminoindene derivative **3a** was carried out in toluene at 115 °C for 24 h in the presence of 10 equiv of 1-phenyl-1-propyne-d_3. Although isomerization of **3a** afforded **4a**, deuterium atoms were not incorporated into **4a**, and 1-phenyl-1-propyne-d_3 was recovered completely. This result indicates that this reaction is an intramolecular isomerization. To elucidate the reaction mode more clearly, we heated a mixture of aminoindene **3b** and deuterated aminoindene **3a′** (eq 2). As a



result, aminoindenes **3b** and **3a′** were isomerized to **4b** and **4a′**. In this reaction, aminoindene derivatives **4b′** and **4a**, which could be produced by intermolecular isomerization, were not

(11) In the presence of a catalytic amount of a rhenium complex, $[ReBr(CO)_3(thf)]_2$, the rate of isomerization was increased and indene isomer **4a** was obtained in 92% yield.

TABLE 1. Solvent Effect on the Yields of Aminoindenes



entry	solvent	% yield[a] 4a	% recov[a] 3a
1	toluene	40	60
2	THF	57	43
3	1,2-dichloroethane	55	45
4	DMF[b]	>99	0
5	acetonitrile	83	17
6	DMSO[c]	>99	0

[a] The yield was determined by ^{1}H NMR with 1,1,2,2-tetrachloroethane as an internal standard. [b] *N*,*N*-Dimethylformamide. [c] Dimethylsulfoxide.

formed. This result also indicates that the isomerization of aminoindenes is an intramolecular version.[12]

Next, we carried out the isomerization reaction using ^{13}C-labeled aminoindene derivative **5a** to investigate the reaction mechanism (eq 3). By heating **5a** at 135 °C for 24 h, isomerization of **5a** proceeded and isomer **6a** was obtained in 82% yield. As a result of ^{13}C NMR measurements, not only

did the interconversion of two substituents, hexyl and phenyl groups, take place but also the interconversion of carbon atoms of the indene framework. This result shows that the carbon−carbon bonds between the indene framework and the substituted groups were not cleaved, and aminoindene derivative **6a** was formed by the rearrangement of the indene framework.

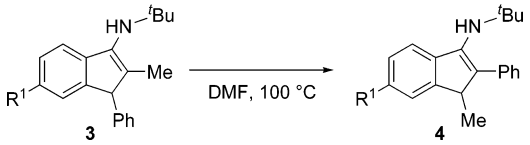
By investigating the reaction temperature in DMF for 24 h, aminoindene **3a** was isomerized even at 25 °C (**4a**: 12% yield; **3a**: 88% recovery).[13] Since isomerizations of indene derivatives via the rearrangement of an indene skeleton usually need harsh conditions or UV irradiation,[9] the fact that the isomerization of **3a** to **4a** proceeds even at room temperature without UV irradiation deserves special mention.

One of the possible mechanisms is that the isomerization of aminoindene **3a** is promoted by light (a fluorescent light or sunlight). By heating aminoindene **3a** in DMF at 50 °C for 24 h in the dark, aminoindene **4a** was formed in 17% yield. This yield is the same as that obtained by heating **3a** at 50 °C for 24 h without shading. The result shows that the isomerization did not proceed by light. Another possible mechanism is that the

(12) The isomerization rates of **3a** to **4a** in *N*,*N*-dimethylformamide at 100 °C for 3 h were changed when the reactions were carried out under different concentrations (**4a**: 43% (0.40 M); 38% (0.20 M); 27% (0.10 M); 18% (0.050 M).). One possible explanation of this result is that **4a** was formed via intramolecular isomerization, which was influenced by the amino group of another molecule. In fact, by adding a base (1.0 equiv) in the reaction mixture, the accelerating effect of the base was observed (0.20 M, none: 38%; aniline: 61%; piperidine: >99%).

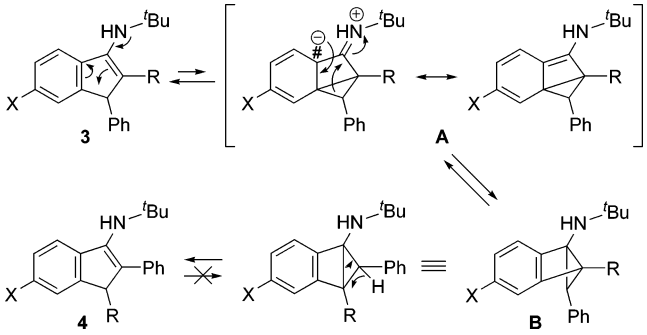
(13) 80 °C (**4a**: 90%; **3a**: 10%); 50 °C (**4a**: 17%; **3a**: 82%).

TABLE 2. Effect of Substituents of Aminoindenes on Isomerization Rate



	R^1 = H		R^1 = MeO	
time/ h	yield [%] **4a**	recov [%] **3a**	yield [%] **4c**	recov [%] **3c**
0.5	16	84	4	96
1	17	83	12	88
3	53	47	35	65
8	87	12	58	42
24	>99	0	>99	0

SCHEME 1. Proposed Mechanism of the Isomerization of Aminoindene Derivative 3



isomerization proceeds via a radical pathway.[14] Addition of such radical inhibitors as 1-dodecene, butyl vinyl ether, 1,4-benzoquinone, and galvinoxyl to the isomerization from aminoindene **3a** to **4a** did not disturb the reaction. This result indicates that the isomerization of **3a** did not proceed via a radical pathway.

We investigated a substituent on the aromatic ring of aminoindenes (Table 2). By heating an aminoindene derivative **3c** that has an electron-donating methoxy group at the *para*-position in DMF at 100 °C, the corresponding aminoindene isomer **4c** was formed. However, the rate of isomerization of **3c** was slightly slow. This result indicates that destabilization by the electron-donating group at the position indicated with sharps (#) in Scheme 1 decreased the reaction rate.

Compared with the previous reports on the indene isomerization, the rearrangement of aminoindene derivatives proceeded under mild conditions. The existence of a nitrogen atom accelerates the rearrangement. By considering the above investigations, the proposed mechanism of isomerization is as follows (Scheme 1): (1) formation of bicyclo[2.1.0]pentenamine intermediate **A** by the flow of electrons from a nitrogen atom and dearomatization; (2) rearrangement of the intermediate **A** to give bicycle[2.1.0]pentane intermediate **B** by rearomatization; (3) production of aminoindene derivative **4**, which is the isomer of **3**, by a ring opening reaction and the rearrangement of a proton. In the last step, the reaction does not proceed in a reverse manner because **4** is thermodynamically more stable than **3**, owing to the conjugation in **4**.

(14) For the theoretical calculations of the isomerization of indene derivatives via radical intermediates, see: Dubnikova, F.; Lifshitz, A. *Isr. J. Chem*. **2003**, *43*, 325.

Summary

We have found that aminoindene derivatives isomerize to the isomers of the aminoindenes under mild reaction conditions. Previously reported indene isomerizations have needed harsh conditions or UV irradiation. From this viewpoint, the fact that the rearrangement proceeds even at room temperature without UV irradiation deserves special mention. The ^{13}C-labeled experiment shows that this isomerization is not just the exchange of two substituents on the indene skeleton; this reaction proceeds via the rearrangement of the indene framework. Since the rearrangement of the indene framework usually occurs under UV irradiation, an amino group is important to promote the rearrangement under mild conditions, and so the rearrangement looks like a thermal version of a UV light-promoted valence isomerization of an indene framework.

Experimental Section

General Procedure for the Isomerization of Aminoindene Derivatives. The mixture of an aminoindene derivative (0.200 mmol) and DMF (1.0 mL) was heated at 100 °C for 24 h. After the solvent was removed in vacuo, the product was isolated by silica gel column chromatography.

***sec*-Phenethylalcohol-*methyl*-^{13}C.**[15] A solution of iodomethane-^{13}C (10 atom % ^{13}C) in anhydrous ether (93.0 mL) was added dropwise to a stirred suspension of dry magnesium turnings (2.62 g, 107 mmol) in anhydrous ether (7.00 mL) (Scheme S1). The resulting mixture was stirred at reflux for 1 h, and a solution of benzaldehyde (10.9 mL, 107 mmol) in anhydrous ether (70.0 mL) was added dropwise at −5 °C. The reaction mixture was gradually warmed to 25 °C, and the reaction mixture was stirred for 2 h. After the mixture was quenched with aq NH_4Cl, washed with brine, and dried with $MgSO_4$. The solution was concentrated in vacuo to give *sec*-phenetylalcohol-*methyl*-^{13}C in 99% yield.

Acetophenone-*methyl*-^{13}C.[16] The mixture of H_5IO_6 (6.48 g, 28.4 mmol) and acetonitrile (160 mL) was stirred vigorously at 25 °C for 15 min (Scheme S1). Then, *sec*-phenetylalcohol-*methyl*-^{13}C (3.14 g, 25.5 mmol) was added to the above mixture at 0 °C, followed by the addition of pyridinium chlorochromate (PCC) (115 mg, 0.538 mmol) in acetonitrile (15 mL) in three portions. After being stirred for 2 h, the reaction mixture was diluted with ethyl acetate (100 mL) and was washed with brine, saturated aq Na_2SO_3, and brine. After the mixture was dried with anhydrous Na_2SO_4 and concentrated, acetophenone-*methyl*-^{13}C was obtained in 65% yield.

Phenylacetylene-α-^{13}C.[17] To a solution of lithium diisopropylamide (which was prepared at 0 °C from diisopropylamine (3.70 mL, 26.4 mmol) and *n*-butyllithium in hexane (1.57 M, 17.0 mL, 26.7 mmol)) in dry THF (30 mL) was added dropwise acetophenone-*methyl*-^{13}C (3.01 g, 25.0 mmol) in THF (13 mL) at −78 °C (Scheme S1). After the mixture was stirred for 1 h, diethyl chlorophosphate (3.99 mL, 27.6 mmol) was added at this temperature. After warming to room temperature gradually, the mixture was added dropwise to a solution of LDA (56.3 mmol) in THF (60 mL), which was prepared at −78 °C as described above. The mixture was warmed to room temperature over 3 h and was quenched with water. The mixture was extracted with pentane, was washed with 1 M HCl, water, and aq $NaHCO_3$, and was dried with $MgSO_4$. After distillation, phenylacetylene-α-^{13}C was obtained in 43% yield.

Phenyl-1-octyne-α-^{13}C.[18] To a solution of *n*-butyllithium in hexane (1.57 M, 7.62 mL, 12.0 mmol) was added phenylacetylene-

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α-^{13}C (1.02 g, 9.97 mmol) in THF (4.0 mL) (Scheme S1). The solution was heated at reflux until gas evolution ceased (3.5 h). Iodohexane (1.62 mL, 11.0 mmol) was added, and the mixture was heated at reflux for 12 h. After cooling, the mixture was quenched with water, was extracted with ether, and was washed with brine. After the mixture was dried with $MgSO_4$ and distilled, phenyl-1-octyne-α-^{13}C was obtained in 73% yield.

***N-tert*-Butyl-2-hexyl-3-phenyl-3*H*-inden-1-amine (5a).**[10] The mixture of aldimine **1a** (0.500 mmol), phenyl-1-octyne-α-^{13}C (0.500 mmol), and $[ReBr(CO)_3(thf)]_2$ (12.7 mg, 0.0150 mmol) in toluene (1.0 mL) was heated at 135 °C for 1 h (eq S1). After the solvent was removed in vacuo, aminoindene **5a** was isolated in 57% yield by silica gel column chromatography.

***N-tert*-Butyl-3,5-diphenyl-2-methyl-3*H*-inden-1-amine (3b).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04 (s, 9H), 2.08 (s, 1H), 4.76 (s, 1H), 7.29−7.34 (m, 4H), 7.38−7.45 (m, 6H), 7.61−7.63 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.3 (1C), 30.8 (3C), 50.8 (1C), 62.5 (1C), 118.0 (1C), 123.7 (1C), 124.7 (1C), 127.0 (1C), 127.2 (2C), 128.0 (2C), 128.7 (1C), 129.8 (3C), 134.3 (1C), 140.7 (1C), 141.8 (1C), 145.7 (1C), 146.2 (1C), 147.0 (1C); IR (nujol, ν/cm^{-1}) 3058 (w), 2724 (w), 1601 (m), 1465 (w), 1377 (w), 1301 (s), 1226 (w), 1155 (m), 1106 (w), 1074 (w), 1022 (w), 880 (w), 760 (s), 721 (m), 697 (s). Anal. Calcd for $C_{26}H_{27}N$: C, 88.34; H, 7.70; N, 3.96. Found: C, 88.26; H, 7.82; N, 3.89.

***N-tert*-Butyl-5-methoxy-2-methyl-3-phenyl-3*H*-inden-1-amine (3c).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.01 (s, 9H), 2.02 (s, 3H), 3.84 (s, 3H), 4.67 (s, 1H), 6.73−6.75 (dd, J = 8.0, 2.3 Hz, 1H), 6.81 (d, J = 2.0 Hz, 1H), 7.30−7.32 (m, 3H), 7.37−7.45 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.2 (1C) 30.8 (3C), 50.8 (1C), 55.5 (1C), 62.1 (1C), 105.5 (1C), 110.3 (2C), 124.1 (1C), 126.9 (1C), 128.0 (2C), 129.7 (2C), 134.1 (1C), 136.3 (1C), 140.0 (1C), 146.7 (1C), 159.7 (1C); IR (nujol, ν/cm^{-1}) 3055 (w), 1604 (w), 1584 (s), 1473 (w), 1440 (w), 1361 (s), 1343 (s), 1285 (s), 1214 (w), 1175 (s), 1067 (w), 1035 (m), 917 (s), 858 (m), 842 (m), 803 (w), 738 (s), 700 (s), 665 (w). Anal. Calcd for $C_{21}H_{25}NO$: C, 82.04; H, 8.20; N, 4.56; O, 5.20. Found: C, 81.87; H, 8.25; N, 4.55.

***N-tert*-Butyl-2,5-diphenyl-3-methyl-3*H*-inden-1-amine (4b).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07 (s, 9H), 1.20−1.22 (d, J = 7.6 Hz, 3H), 3.90−3.92 (m, 1H), 7.25−7.33 (m, 4H), 7.37−7.54 (m, 6H), 7.63−7.66 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.8 (1C), 31.0 (3C), 44.3 (1C), 54.8 (1C), 120.2 (1C), 121.4 (1C), 125.4 (1C), 126.4 (1C), 126.8 (1C), 127.2 (3C), 128.3 (1C), 128.7 (3C), 128.9 (1C), 137.1 (1C), 138.0 (1C), 139.6 (1C), 140.1 (1C), 141.7 (1C), 143.7 (1C), 148.4 (1C); IR (nujol, ν/cm^{-1}) 2721 (w), 1598 (m), 1464 (w), 1377 (w), 1220 (w), 1198 (s), 1156 (w), 1072 (w), 888 (s), 840 (m), 759 (m), 725 (m), 710 (w), 673 (s), 659 (s). Anal. Calcd for $C_{26}H_{27}N$: C, 88.34; H, 7.70; N, 3.96. Found: C, 88.26; H, 7.76; N, 3.84.

***N-tert*-Butyl-5-methoxy-2-phenyl-3-metheyl-3*H*-inden-1-amine (4c).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05 (s, 9H), 1.16 (d, J = 7.6 Hz, 3H), 3.79−3.88 (m, 1H), 3.85 (s, 3H), 6.85 (dd, J = 8.4, 2.4 Hz, 1H), 7.00 (s, 1H), 7.23−7.25 (m, 1H), 7.33−7.43 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.0 (1C), 30.9 (3C), 44.0 (1C), 54.7 (1C), 55.5 (1C), 109.1 (1C), 111.4 (1C), 120.5 (1C), 126.1 (1C), 128.3 (2C), 128.8 (2C), 136.9 (1C), 137.2 (1C), 137.3 (1C), 140.6 (1C), 149.6 (1C), 157.9 (1C); IR (nujol, ν/cm^{-1}) 3853 (w), 3750 (w), 3734 (w), 3675 (w), 3648 (w), 2724 (s), 1549 (m), 1457 (s), 1376 (s), 1217 (w), 722 (w). HR-MS Calcd for $C_{21}H_{26}ON$ ($[M + H]^+$): 308.2014; Found: 308.2021.

***N-tert*-Butyl-2-hexyl-3-phenyl-3*H*-inden-1-amine (5a).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.83 (t, J = 7.0 Hz, 3H), 0.99 (s, 9H), 1.19−1.30 (m, 4H), 1.50−1.60 (m, 4H), 2.41 (t, J = 7.8 Hz, 2H), 4.64 (s, 1H), 7.17−7.23 (m, 1H), 7.27−7.32 (m, 5H), 7.37−7.40 (m, 2H), 7.53−7.55 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0 (1C), 22.6 (1C), 25.9 (1C), 28.8 (2C), 29.5 (2C), 30.6 (3C), 31.5 (1C), 50.7 (1C), 63.1 (1C), 119.5 (1C), 123.6 (1C), 125.3 (1C), 126.9 (1C), 127.1 (1C), 128.0 (1C), 129.7 (2C), 136.7 (1C), 138.9 (1C), 144.1 (1C) 145.7 (1C) 148.4 (1C); IR (nujol, ν/cm^{-1}) 3853 (m), 3750 (m), 3744 (m), 3675 (m), 3648 (m), 3057 (m), 2857 (w), 1733 (m), 1700 (m), 1652 (m), 1609 (s), 1521 (s), 1558 (m), 1465 (m), 1419 (s), 1362 (w), 1225 (m), 1113 (m), 1027 (w), 757 (w), 737 (s) 700 (s). Anal. Calcd for $C_{25}H_{33}N$: C, 86.40; H, 9.57; N, 4.03. Found: C, 86.15; H, 9.60; N, 4.10.

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Supporting Information Available: Scheme for the preparation of ^{13}C-labeled aminoindene derivative **5a**, ^{13}C NMR spectra of the ^{13}C-labeled aminoindene derivatives **5a** and **6a**, and copies of NMR spectra for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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