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Amino-Claisen Rearrangement. V.[1] Rearrangement of Substituted Tetrahydroquinolines Involving Competitive Cope Rearrangement in a Reaction Intermediate

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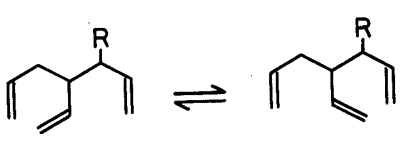
A competitive Cope rearrangement was observed during Claisen rearrangement of substituted tetrahydroquinolines. It was found that the introduction of an ethyl group onto the methylene of the migrating allylic moiety greatly accelerated the Cope rearrangement. At the same time, replacement of the 1-ethyl-2-propenyl group on the aromatic ring by a 1-propenyl (allyl) group was observed.

Keywords——amino-Claisen rearrangement; Cope rearrangement; 1-allyl-8-(1-ethyl-propenyl)-1,2,3,4-tetrahydroquinoline; 8-allyl-1-(2-butenyl)-1,2,3,4-tetrahydroquinoline; allylic group replacement; [3,3] sigmatropic rearrangement

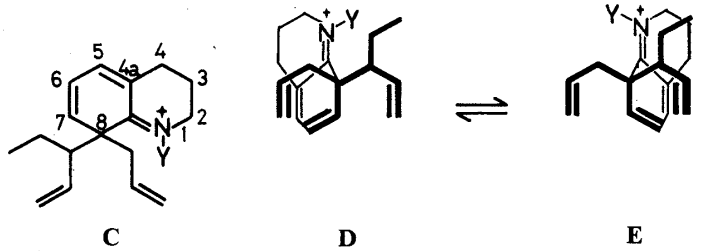
In the aromatic N-Claisen rearrangement,[1] the allyl group on the nitrogen atom of an aniline nucleus having substituents on both *ortho* positions migrates, *via* both *ortho* sites, to the *para* position sigmatropically. If an allylic group is introduced at one of the two *ortho* sites, competitive Cope rearrangement (as shown in Chart 1) can occur, and thus the effects of the substituent R upon the Cope rearrangement[2] can be investigated. In this type of N-Claisen rearrangement, replacement of the initial *ortho* allylic group with the other allylic group should be able to occur. Thus, we selected **3** as model compounds, since the skeleton has been well-studied.[1c,d] The reaction of **3** should lead to the intermediate C (Chart 2) as one of two reaction pathways, and competitive Cope reaction can occur in the intermediates D and E, which are readily interconvertible by flipping of the six-membered ring. Aromatization after the rearrangement should provide the driving force for this reaction.

The compounds **3** and the expected rearrangement products **6** were prepared as shown in Chart 3. The compounds **6** were hydrogenated to **7** and its carbon framework was confirmed by independent synthesis of **7a** from **2b**. The compounds **4** were obtained as by-products in the reaction of **1**. The results of the rearrangements are summarized in the Table. The reaction products were analyzed by gas liquid chromatography (GLC), separated by flush column chromatography[3] and identified by thin layer chromatography (TLC), GLC, infrared (IR) spectroscopy and nuclear magnetic resonance (NMR) spectroscopy. The possible reaction



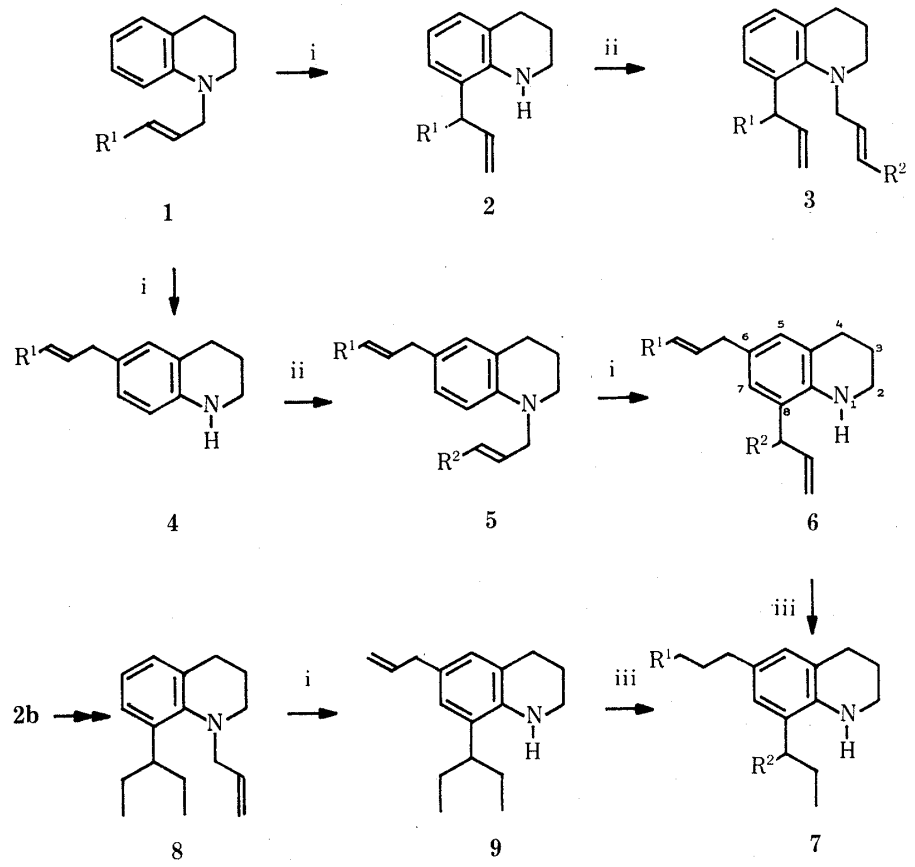
A B

Chart 1



C D E

Chart 2



a : R^1=H, R^2=Et
b : R^1=Et, R^2=H

i) $BF_3 \cdot Et_2O$/150—180 °C/2—3 h,
ii) $R^2CH=CH-CH_2Br$/MeCN/Na_2CO_3/rt,
iii) 5%Pd–C/H_2/EtOH

Chart 3

TABLE

No.	Substrate	R.C.[a]	Crude Y (%)	Products (%)[b]			
				6a	**6b** (*E*/*Z*)	**3**	Others
1	**3a**	A	92.2	<0.1	92.1 (82/18)	1.5	2.7, 1.0, 2.5
2	**3b**	A	84.7	34.9	61.6 (89/11)	—	2.9
3	**3b**	B	72.5	22.8	46.0 (96/4)	8.2	5.8, 13.1

a) Reaction conditions. A: A mixture of **3** (1 mmol) and boron trifluoride etherate (2.1 mmol) was heated at 140 °C for 2 h. B: A solution of **3** (1 mmol) in 2 N sulfuric acid in glycerol–water (2/1, 4 ml) was refluxed (bath temperature 140 °C) for 2 h.
b) The products were analyzed by GLC–15% QF-1 (glass, 3 mm × 2 m), 200 °C, N_2 (30 ml/min); 10% SE-30 (glass, 3 mm × 2 m), 220 °C, N_2 (30 ml/min).

pathways are depicted in Chart 4, in which Y denotes boron trifluoride under reaction condition A and a proton under condition B. Provided that the ratios of the reaction products reflects the differences of the reaction rates, the following conclusions can be drawn. 1) Compound **3a** rearranges *via* pathways a and b, of which route a produces **6b** *via* F. On the other hand, route b gives the intermediate C which has two further reaction pathways, e

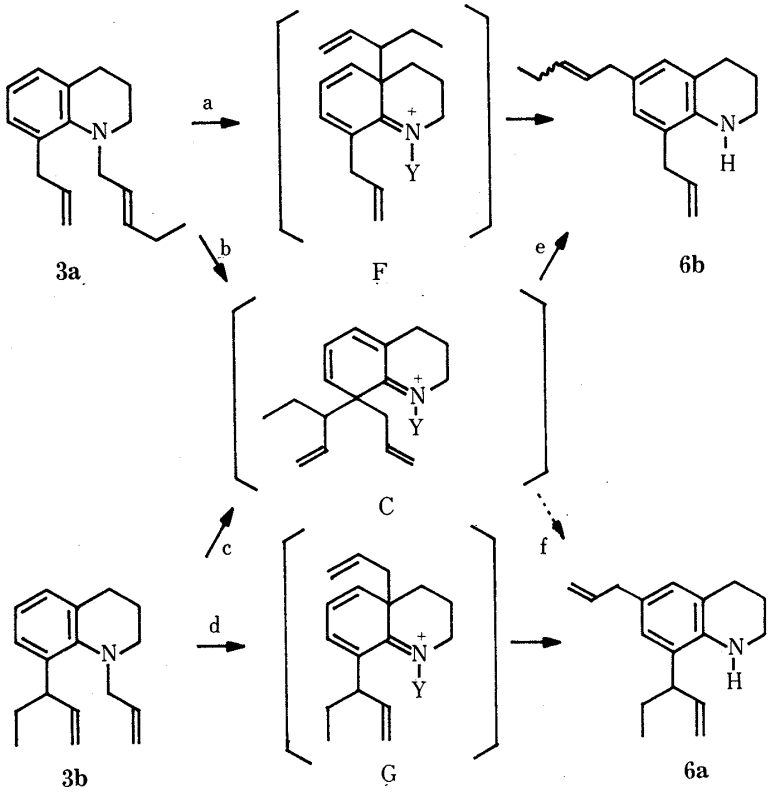


Chart 4

leading to **6b**, and f leading to **6a**. The fact that **6b** was the exclusive product in the rearrangement of **3a** indicates that **3a** also rearranges *via* b, but intermediate C gives **6b** exclusively *via* route e, and route f is virtually non-existent. This behavior of intermediate C suggests that intermediate E (type B, R = Et) is overwhelmingly preferred over D (type A, R = Et). Since the detected amount of the product **6a** was less than 0.1% in the rearrangement of **3a**, the presence of an ethyl group at the allylic methylene accelerates the Cope rearrangement at least a thousand times. This difference of reaction rates corresponds to *ca.* 4 kcal/mol free energy difference. 2) The reaction of **3b** *via* route c should provide the product **6b** exclusively through the intermediate C and the reaction *via* d should give the product **6a** through G. Thus the product ratio **6a**/**6b** in the rearrangement of **3b** represents the rate difference between the reaction pathways d and c. 3) Since the product **6b** was a mixture of geometrical isomers, the rearrangements of **3** should involve boat-like transition states at either one of the two reaction steps as noted in other cases.[1,4] The rearrangement of **3b** under condition B (2 N sulfuric acid) was slow and produced some hydrated materials. There was a slight change in the product ratio **6a**/**6b**. The replacement of the 1-ethyl-2-propenyl group at position 8 by the 2-propenyl (allyl) group during the [3,3] sigmatropic rearrangement of **3b** is the first reported example of replacement of the allylic substituent on an aromatic ring by another allylic group during Claisen rearrangement. This observation suggests that the introduction of a readily migratable allylic moiety at a suitable site may make it possible to detect the route of migration of the allyl group during [3,3] sigmatropic rearrangement. The observed acceleration of the reaction by an ethyl substituent on the allylic moiety should not be due to a steric effect because the ethyl substituent can take the stable equatorial configuration in the transition states during the reaction of **3**. Since the steric effect of the ethyl substituent is small, the transition state should resemble the product, so the stability of the final product may be the major driving force for these reactions.

Experimental[5)]

1-((*E*)-2-Pentenyl)-1,2,3,4-tetrahydroquinoline (1b)——A solution of 1,2,3,4-tetrahydroquinoline (THQ) (5.1 g, 38.3 mmol), 2-pentenyl bromide[6)] (8.2 g, 55.0 mmol) and sodium carbonate (2.1 g, 19.8 mmol) in acetonitrile (50 ml) was stirred at room temperature (rt) for 14 h, then refluxed for 1 h. Evaporation, basification with sodium hydroxide and extraction with ether (three times) gave the crude product (7.23 g), which was distilled to give **1b** (4.06 g, 52.7% yield), *E*:*Z*=97:3 on GLC (10% SE-30; 200 °C; N_2 30 ml/min). Liquid, bp 111—113 °C/2 mmHg. MS *m/z*: 201 (M^+, 54%), 172 (51), 146 (59), 132 (60), 129 (P^+). IR ν_{max}^{film} cm^{-1}: 3070, 1660, 970, 768. NMR δ: 0.93 (3H, t, *J*=7 Hz, $CH_2C\underline{H}_3$), 1.66—2.25 (4H, m, C-3-H+=CH–$C\underline{H}_2$–Me), 2.70 (2H, t, *J*=6 Hz, C-4-H), 3.20 (2H, t, *J*=5.5 Hz, C-2-H), 3.75 (2H, d, *J*=4.5 Hz, N–$C\underline{H}_2$–CH=. Singlet when irradiated at δ 5.50), 5.29 (1H, td, *J*=4.5, 15.5 Hz, N–CH_2–$C\underline{H}\overset{E}{=}C\underline{H}$–Et. Doublet *J*=15.5 Hz on irradiation at δ 3.75), 5.71 (1H, td, *J*=5, 15.5 Hz, N–$CH_2C\underline{H}\overset{E}{=}C\underline{H}$–Et. Doublet, *J*=15.5 Hz when irradiated at δ 1.96), 6.36—7.03 (4H, m, Ar–H). *Anal.* Calcd for $C_{14}H_{19}N$: C, 83.53; H, 9.51; N, 6.96. Found: C, 83.40; H, 9.68; N, 6.74.

8-(1-Ethyl-2-propenyl)-1,2,3,4-tetrahydroquinoline (2b) and 6-(2-Pentenyl)-1,2,3,4-tetrahydroquinoline (4b)——A mixture of **1b** (2.065 g, 10.3 mmol) and boron trifluoride etherate (2.6 ml, 21.1 mmol) was heated at 150 °C for 3 h. The reaction mixture was basified with 1 N sodium hydroxide and extracted with ether (3×10 ml). The crude product (1.889 g) was chromatographed on silica gel (60 g) with benzene, giving **2b** (1.346 g, 65.2%) then **4b** (0.304 g, 14.7% yield). The reaction in 2 N sulfuric acid in glycerol–water (2/1) at 140 °C (bath temperature) for 4 h gave only **2b** in 49% yield. **2b**: Liquid. MS *m/z*: 210 (M^+, 67%), 186 (20), 172 (P^+), 144 (60). IR ν_{max}^{film} cm^{-1}: 3420, 1632, 912, 745. NMR δ: 0.90 (3H, t, *J*=7 Hz, $CH_2C\underline{H}_3$), 1.72 (2H, quintet, *J*=7 Hz, CH–$C\underline{H}_2$–Me), 1.85 (2H, quintet, *J*=6 Hz, C-3-H), 2.73 (2H, t, *J*=6 Hz, C-4-H), 3.03 (1H, m, CH=CH–$C\underline{H}$–Et. Doublet, *J*=7 Hz when irradiated at δ 1.72), 3.23 (2H, t, *J*=5.5 Hz, C-2-H), 3.80 (1H, br, NH), 4.83, 4.93 and 5.10 (2H, each m, CH–CH=$C\underline{H}_2$), 5.53—6.10 (1H, m, CH–$C\underline{H}$=CH_2), 6.43—7.00 (3H, m, Ar–H). Picrate: Yellow needles, mp 134—135 °C (EtOH). *Anal.* Calcd for $C_{20}H_{22}N_4O_7$: C, 55.81; H, 5.15; N, 13.12. Found: C, 56.04; H, 4.93; N, 13.20. **4b**: Liquid. MS *m/z*: 201 (M^+, 6%), 197 (51), 168 (P^+), 142 (20). IR ν_{max}^{film} cm^{-1}: 3400, 1690, 1610, 965, 810. NMR δ: 0.97 (3H, t, *J*=7 Hz, CH_2–$C\underline{H}_3$), 1.6—2.2 (4H, m, $C\underline{H}_2$–Me+C-3-H), 2.68 (2H, t, *J*=6 Hz, C-4-H), 3.13 (2H, m, Ar–$C\underline{H}_2$–CH=), 3.20 (2H, t, *J*=5.5 Hz, C-2-H), 3.37 (1H, br, NH), 5.48 (2H, m, CH_2–$C\underline{H}$=$C\underline{H}$–Et), 6.39 (1H, d, *J*=9 Hz, C-8-H), 6.73 (1H, br s, C-5-H), 6.74 (1H, br d, *J*=9 Hz, C-7-H).

8-Allyl-1-((*E*)-2-pentenyl)-1,2,3,4-tetrahydroquinoline (3a)——A mixture of 8-allyl-THQ hydrochloride (640 mg, 4.1 mmol),[1d)] 2-pentenyl bromide (640 mg, 4.4 mmol) and sodium carbonate (498 mg, 4.7 mmol) in acetonitrile (22 ml) was reacted as described for **1b**. The crude product (966 mg) was purified by chromatography (silica gel 45 g, benzene), giving 860 mg (88.1% yield) of **3a** as a liquid, *E*:*Z*=99.4:0.6. MS *m/z*: 241 (M^+), 179 (P^+). IR ν_{max}^{film} cm^{-1}: 3075, 1668, 1640, 967, 910, 763. NMR δ: 1.03 (3H, t, *J*=7 Hz, CH_2–$C\underline{H}_3$), 1.53—2.23 (4H, m, $C\underline{H}_2$–Me+C-3-H), 2.80 (2H, t, *J*=6.5 Hz, C-4-H), 3.07 (2H, m, C-2-H), 3.36 (2H, d, *J*=4 Hz, N–$C\underline{H}_2$–CH=), 3.43 (2H, td, *J*=1.5, 6 Hz, Ar–$C\underline{H}_2$–CH=CH_2), 5.00 and 5.23 (2H, each m, Ar–CH_2–CH=$C\underline{H}_2$), 5.70 (2H, m, CH_2–$C\underline{H}$=$C\underline{H}$–Et), 6.03 (1H, tdd, *J*=6, 9, 17 Hz, Ar–CH_2–$C\underline{H}$=CH_2. Doubly d, *J*=9, 17 Hz when irradiated at δ 3.43), 6.97 (3H, m, Ar–H).

1-Allyl-8-(1-ethyl-2-propenyl)-1,2,3,4-tetrahydroquinoline (3b)——The reaction of **2b** (0.803 g, 4.0 mmol), allyl bromide (2.028 g, 16.8 mmol) and sodium carbonate (1.0 g, 9.4 mmol) in acetonitrile (20 ml), followed by flush column chromatography (silica gel 4×14 cm) of the crude product (0.944 g) with petroleum ether (PE)–ethyl acetate (EA) (98:2), gave 0.624 g (64.8% yield) of **3b** as a liquid. IR ν_{max}^{film} cm^{-1}: 3080, 1638, 915, 756. NMR δ: 0.83 (3H, t, *J*=7 Hz, CH_2–$C\underline{H}_3$), 1.43 (2H, quintet, *J*=7 Hz, CH–$C\underline{H}_2$–Me), 1.73 (2H, m, C-3-H), 2.73 (2H, t, *J*=6.5 Hz, C-4-H), 2.97 (2H, m, C-2-H), 3.37 (2H, d, *J*=4 Hz, with small couplings, $C\underline{H}_2$–CH=CH_2. Singlet on irradiation at δ 5.90), 3.57 (1H, q, *J*=7 Hz, CH_2=CH–$C\underline{H}$–Et. Doublet, *J*=7 Hz, on irradiation at δ 1.63), 4.83, 5.10, 5.27 and 5.46 (4H, each m, $C\underline{H}_2$=CH–CH–Et+CH_2–CH=$C\underline{H}_2$), 5.7—6.3 (2H, m, CH_2=$C\underline{H}$–CH–Et+CH_2–$C\underline{H}$=CH_2), 6.8—7.0 (3H, m, Ar–H). Hydrobromide: mp 187.5—188 °C (MeOH). *Anal.* Calcd for $C_{17}H_{24}BrN$: C, 63.35; H, 7.51; N, 4.35. Found: C, 63.18; H, 7.76; N, 4.18.

6-Allyl-1-((*E*)-2-pentenyl)-1,2,3,4-tetrahydroquinoline (5a)——The reaction of **4a** (221 mg, 1.3 mmol), 2-pentenyl bromide (239 mg, 1.6 mmol) and sodium carbonate (72 mg, 0.68 mmol) in acetonitrile (8 ml), followed by chromatography (silica gel 6.0 g, benzene), gave **5a** (180 mg, 58.5% yield) as a liquid. MS *m/z*: 241 (M^+, 91%), 214 (41), 186 (62), 173 (80), 169 (P^+), 130 (35). IR ν_{max}^{film} cm^{-1}: 3080, 1665, 1640, 1618, 970, 910, 802. NMR δ: 0.97 (3H, t, *J*=7 Hz, CH_2–$C\underline{H}_3$), 1.73—2.27 (4H, m, C-3-H+=CH–CH_2–Me), 2.75 (2H, t, *J*=6 Hz, C-4-H), 3.20 (2H, t, *J*=5.5 Hz, C-2-H), 3.27 (2H, d, *J*=6 Hz, $C\underline{H}_2$–CH=CH_2), 3.83 (2H, d, *J*=4 Hz, $C\underline{H}_2$–CH=CH–Et), 4.93 and 5.03 (2H, each m, CH_2–CH=$C\underline{H}_2$), 5.60 (2H, m, CH_2–$C\underline{H}$=$C\underline{H}$–Et), 6.00 (1H, tdd, *J*=6, 9, 17 Hz, CH_2–$C\underline{H}$=CH_2), 6.59 (1H, d, *J*=8 Hz, C-8-H), 6.80 (1H, br s, C-5-H), 6.86 (1H, dd, *J*=2, 8 Hz, C-7-H).

1-Allyl-6-(2-pentenyl)-1,2,3,4-tetrahydroquinoline (5b)——**5b** was prepared from **4b** in 69.4% yield as described for **3b**. *E*:*Z*=92:8. **5b**: Liquid. IR ν_{max}^{film} cm^{-1}: 3080, 1640, 1610, 963, 915, 795. NMR δ: 1.00 (3H, t, *J*=7 Hz, CH_2–$C\underline{H}_3$), 1.70—2.27 (4H, m, =CH–$C\underline{H}_2$–Me+C-3-H), 2.75 (2H, t, *J*=6 Hz, C-4-H), 3.18 (2H, d with small couplings, *J*=4.5 Hz, $C\underline{H}_2$–CH=CH–Et), 3.23 (2H, t, *J*=5.5 Hz, C-2-H), 3.83 (2H, td, *J*=1.5, 4.5 Hz, $C\underline{H}_2$–CH=CH_2), 5.03 and 5.30 (2H, each m, CH_2–CH=$C\underline{H}_2$), 5.53 (2H, m, CH_2–$C\underline{H}$=$C\underline{H}$–Et), 5.87 (1H, tdd, *J*=4.5, 9, 17.5 Hz, CH_2–

CH=CH_2), 6.50 (1H, d, J=8 Hz, C-8–H), 6.83 (1H, s, C-5–H), 6.90 (1H, br d, J=8 Hz, C-7–H).

6-Allyl-8-(1-ethyl-2-propenyl)-1,2,3,4-tetrahydroquinoline (6a)——The reaction of **5a** (97 mg, 0.4 mmol) with boron trifluoride etherate (0.11 ml, 0.9 mmol) at 140 °C for 2 h, followed by purification of the crude product by flush column chromatography as described for **2b** gave **6a** as a liquid. MS m/z: 241 (M^+), 171 (P^+). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3430, 3080, 1637, 995, 815. NMR δ: 0.93 (3H, t, J=7 Hz, CH_2–CH$_3$), 1.76 (2H, quintet, J=7 Hz, CH_2=CH–CH–CH$_2$–Me), 1.90 (2H, quintet, J=6 Hz, C-3–H), 2.77 (2H, t, J=6 Hz, C-4–H), 3.23 (2H, d, J=6 Hz, CH$_2$–CH=CH_2), 3.00—3.37 (3H, m, C-2–H+CH_2=CH–CH–Et), 3.77 (1H, br, NH), 4.90 and 5.27 (2H, each m, CH_2–CH=CH$_2$), 5.56—6.30 (2H, m, CH_2–CH=CH_2+CH_2=CH–CH–Et), 5.17 (2H, s, CH$_2$=CH–CH–Et), 6.70 (2H, s, Ar-H). A trace of **6b** (1.2%) was detected in the purified specimen by GLC.

8-Allyl-6-(2-pentenyl)-1,2,3,4-tetrahydroquinoline (6b)——The reaction of **5a** as described for **1b** gave **6b** in 66.7% yield, E:Z=97:3 on GLC (15% QF-1). **6b**: Liquid. IR ν_{max}^{film} cm^{-1}: 3425, 3080, 1633, 976, 913. NMR δ: 0.93 (3H, t, J=7 Hz, CH_2–CH$_3$), 1.56—2.23 (4H, m, =CH–CH$_2$–Me+C-3–H), 2.73 (2H, m, t, J=6 Hz, C-4–H), 3.16 (4H, m, CH$_2$–CH=CH_2+CH$_2$–CH=CH–Et), 3.23 (2H, t, J=5.5 Hz, C-2–H), 3.67 (1H, br, NH), 4.93 and 5.17 (2H, each m, CH_2–CH=CH$_2$), 5.50 (2H, m, CH_2–CH=CH–Et), 5.93 (1H, tdd, J=6, 9, 17.5 Hz, CH_2–CH=CH_2), 6.63 (2H, s, Ar–H). A trace of **6a** was detected in the crude product (1.5%) by GLC analysis.

8-(1-Ethylpropyl)-6-propyl-1,2,3,4-tetrahydroquinoline (7a)——a) A solution of **6a** (62 mg) and 5% Pd–C (20 mg) in methanol was hydrogenated in an atmosphere of hydrogen. The catalyst was removed and the filtrate was evaporated to give **7a** (57 mg, 92% yield).

b) The similar reduction of **9** (190 mg), followed by column chromatography (silica gel 6 g, benzene), gave **7a** (134 mg, 76.5% yield). **7a**: Liquid. IR ν_{max}^{film} cm^{-1}: 3450, 1610, 1490. NMR δ: 0.77 (6H, t, J=7 Hz, CH–CH_2–CH$_3$×2), 0.85 (3H, t, J=7 Hz, CH_2CH_2CH$_3$), 1.20—2.10 (8H, m, C-3–H+CH–CH$_2$–Me×2+CH_2CH$_2$–Me), 2.33 (1H, m, Ar–CH–Et_2), 2.40 (2H, t, J=6 Hz, Ar–CH$_2$–Et), 2.72 (2H, t, J=6 Hz, C-4–H), 3.25 (2H, t, J=5.5 Hz, C-2–H), 3.29 (1H, s, NH), 6.73 (2H, s, Ar–H). Picrate: mp 180—182 °C (dec.) (CH_2Cl_2–EtOH).

6-Pentyl-8-propyl-1,2,3,4-tetrahydroquinoline (7b)——Catalytic hydrogenation of **6b** over 5% Pd–C as described above gave **7b** as a liquid. IR ν_{max}^{film} cm^{-1}: 3440, 1614, 1490, 1312, 881. NMR δ: 0.90 (6H, t, J=6.5 Hz, CH_2–CH$_3$×2), 2.2—2.6 (4H, m, Ar–CH$_2$–R×2), 2.72 (2H, t, J=6 Hz, C-4–H), 3.26 (2H, t, J=5.5 Hz, C-2–H), 3.37 (1H, br, NH), 6.63 (2H, s, Ar–H). Picrate: mp 138—139.5 °C (EtOH).

1-Allyl-8-(1-ethylpropyl)-1,2,3,4-tetrahydroquinoline (8)——The catalytic reduction product (1.157 g) of **2b** (1.611 g) was purified by flush column chromatography (silica gel 88 g, PE–EA=97:3) to give 8-(1-ethylpropyl)-1,2,3,4-tetrahydroquinoline as a liquid. MS m/z: 203 (M^+, 36%), 174 (P^+), 146 (36%). IR ν_{max}^{film} cm^{-1}: 3450, 1597, 1495, 740. NMR δ: 0.83 (6H, t, J=7 Hz, CH_2–CH$_3$×2), 1.63 (4H, quintet, J=7 Hz, Ar–CH–CH$_2$–Me×2), 1.90 (2H, m, C-3–H), 2.40 (1H, quintet, J=6.5 Hz, Ar–CHEt_2), 2.80 (2H, t, J=6 Hz, C-4–H), 3.33 (2H, t, J=5.5 Hz, C-2–H), 3.50 (1H, br s, NH), 6.4—6.9 (3H, m, Ar–H). This product (0.903 g) was treated with allyl bromide in the manner described above, and purification of the crude product (0.703 g) by column chromatography (silica gel 22.0 g, benzene) gave **8** (0.574 g, 53% yield) as a liquid. IR ν_{max}^{film} cm^{-1}: 3050, 1642, 920. NMR δ: 0.80 (6H, t, J=7 Hz, CH_2–CH$_3$×2), 1.3—2.0 (6H, m, CH$_2$–Me×2+C-3–H), 2.83 (2H, t, J=6 Hz, C-4–H), 3.03 (2H, m, C-2–H), 3.47 (2H, td, J=1.5, 6 Hz, CH$_2$–CH=CH_2), 5.13, 5.26 and 5.50 (2H, each m, CH_2–CH=CH$_2$), 6.03 (1H, tdd, J=6, 9, 18 Hz, CH_2–CH=CH_2), 6.83—7.06 (3H, m, Ar–H). Picrate: mp 117—118 °C (EtOH). *Anal.* Calcd for $C_{23}H_{28}N_4O_7$: C, 58.47; H, 5.97; N, 11.86. Found: C, 58.21; H, 6.09; N, 11.79.

6-Allyl-8-(1-ethylpropyl)-1,2,3,4-tetrahydroquinoline (9)——The reaction of **8** (252 mg, 1.0 mmol) and boron trifluoride (0.25 ml, 2.0 mmol) at 150 °C for 2 h, followed by purification of the crude product by chromatography (silica gel 7 g, benzene), afforded **9** (140 mg, 55.5% yield) as a liquid. MS m/z: 245 (M^++2, 24%), 243 (M^+, 73%), 214 (P^+). IR ν_{max}^{film} cm^{-1}: 3450, 3080, 1640, 915. NMR δ: 0.83 (6H, t, J=7 Hz, CH_2–CH$_3$×2), 1.50 (4H, quintet, J=7 Hz, Ar–CH–CH_2–Me×2), 1.90 (2H, m, C-3–H), 2.38 (1H, quintet, J=6.5 Hz, Ar–CHEt_2), 2.80 (2H, t, J=6.5 Hz, C-4–H), 3.26 (d, J=6 Hz, CH$_2$–CH=CH_2), 3.33 (2H, t, J=5.5 Hz, C-2–H), 3.63 (1H, br, NH), 4.90 and 5.10 (2H, each m, CH_2–CH=CH$_2$), 5.97 (1H, tdd, J=6, 9, 18 Hz, CH_2–CH=CH_2), 6.67 (2H, s, Ar–H). The rearrangement of **8** in 2 N sulfuric acid in glycerol–water (2/1) at 140 °C (bath temperature)[1c] for 6 h gave **9** in 13.1% yield along with complex polar products.

Rearrangement of 3a——A mixture of **3a** (244 mg, 1.0 mmol) and boron trifluoride etherate (0.25 ml, 2.0 mmol) was heated at 140 °C for 2 h. The brown reaction mixture was treated with excess 1 N sodium hydroxide then extracted with ether three times to give the crude product (225 mg), which was separated by flush column chromatography (silica gel 24 g, PE:EA=95:5) to afford **6b** (177 mg, 72.5% yield). Detailed analysis of the separated fractions by GLC, TLC and NMR spectroscopy indicated the presence of **6a**, but its content in the crude product was calculated to be less than 0.1%.

Rearrangement of 3b——a) A mixture of **3b** (198 mg, 0.8 mmol) and boron trifluoride (0.22 ml, 1.8 ml) was heated at 140 °C for 2.5 h. The crude product (168 mg) was flush-chromatographed on silica gel (24 g) with PE:EA (95:5). The first eluate gave a product (24 mg, 12.1% yield) identical with **6a**. The second eluate (19 mg) yielded a mixture of **6a** and **6b** (81:16) and the third eluate gave **6b** (69 mg, 34.8% yield, 89.6% purity, E:Z=98:2).

b) A solution of **3b** (222 mg, 0.9 mmol) in 2 N sulfuric acid in glycerol–water (2/1, 4 ml) was refluxed (bath temperature 140 °C) for 2 h. The reaction mixture was basified with 1 N sodium hydroxide then extracted with ether

three times. The crude product (161 mg) was chromatographed (silica gel 60 g, benzene) to give a mixture (3.4 mg) of **4a**, **6a** and **6b** (8 : 44 : 47), **3b** (9.4 mg) and **6b** (29 mg, 13.1% yield, 92% purity, $E:Z=96:4$). The identifications were carried out by TLC, GLC, GC-MS and NMR spectroscopy.

References and Notes

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