Carbolithiation of styrenes with *N-tert*-butyl aldimines

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The addition of aldimine anions to styrene occurs upon the treatment of *N-tert*-butyl aldimine with LDA followed by the addition of styrene to give the corresponding aldehyde after hydrolysis. Cyclohexenyl amines are generated when the reactions are performed with unsaturated aldimines. This approach affords 4-phenyl substituted butanals and cyclohexenyl amines in a simple and inexpensive way.

Keywords: C2-Elongation, carbolithiation, aldimine anion, styrene, cycloalkenylation

C2-Elongation by the chemistry of α-deprotonated aldimines finds broad applications in organic chemistry.[1] The aldimines deprotonated with a base (Stork's approach[2]) or specifically with LDA (Wittig's approach[3]) react with an electrophile, usually an alkyl halide in most cases, to give the α-alkylated products.

In view of reagent and environmental costs, the use of a simple alkene instead of an alkyl halide is desirable. In the exploration of the area, Nakamura and coworkers reported[4] an enantioselective synthesis of α-alkylated cyclohexanones through three-component coupling of an optically active zinc enamide with alk-1-enes and an electrophile. The key step involves the addition of a zinc enamide to an unreactive alkene. Matsubara and Kobayashi reported[5] that $Cu(OTf)_2$-catalysed stereoselective carbon–carbon and carbon–nitrogen formation by reaction of N-acylimino esters, glyoxylates, aldehyde-ketone derivatives and iminophosphates with enamides and enecarbamates which act as nucleophiles. The reaction proceeds by a non-concerted aza-ene type pathway which is facilitated by Cu-coodination between N-, O- or P-atoms on the substrates.

In the meantime, carbolithiation enjoys widespread use in the chemistry of carbon–carbon bond formation.[6–9] This reaction involves the addition of alkyl, vinyl and aryllithiums to unactivated alkenes and alkynes, and can be viewed as a subset of the broader family of carbometallation reactions.[10,11]

In spite of the wide range of applications of carbolithiation in organic synthesis, the addition of lithiated aldimine anions to alkenes has received relatively little attention. Marazano and coworkers reported[12] that deprotonated *N-tert*-butyl aldimines react with vinamidinium chloride to give 2-alkylaminopentadienimine derivatives, which are efficient intermediates for the preparation of 3-substituted pyridines and the corresponding hydrochloride salts. Other examples are the addition of the lithiated *N*-isobutylidene-*tert*-butylamine to 1,3-dienes (butadiene, isoprene and myrcene) or an unsaturated aldehyde in relatively low yield and limited substrate scope.[13,14] We now report a convenient approach to the preparation of 4-phenyl substituted butanals and cyclohexenylamines via the addition of *tert*-butyl aldimine anions to styrene.

Results and discussion

In our exploration of efficient C–C-bond forming reactions in the field of fragrance chemistry, we found that the lithiated aldimine **1** reacted with styrene to give addition product **3** which was in turn transformed to **4** after hydrolysis as shown in Scheme 1.

Albeit the newly formed aldimine **3** can be isolated in pure form, further transformation to aldehyde **4** could be achieved in a one-pot reaction upon treatment of the quenched aqueous solution with oxalic acid and gave the 4-phenyl substituted butanal **4** in a simple and inexpensive way. The products obtained from the addition of different lithiated aldimines to styrenes are tabulated in Table 1.

Double-addition compound **12** was produced when the shorter chain aldimine **5** was subjected to the carbolithiation conditions (entry 1 in Table 1). Mono-addition product **13** was obtained when the sterically more hindered aldimine **6** was used (entry 2 in Table 1). The reaction of ketimine **7** with styrene (entry 3 in Table 1) gave product **14** as a consequence of α-alkylation of the lithium ketimine. The reaction of α-methylstyrene **9** with the aldimine anion was sluggish and could only be slightly improved when the reaction was carried out in the presence of 1 equiv. of TMEDA (entry 4 in Table 1). Product **15** was isolated in 30% yield after hydrolysis of the reaction mixture, but the reaction of 2-methylstyrene **10** with **8** afforded a good yield of **16** as shown in entry 5 in Table 1.

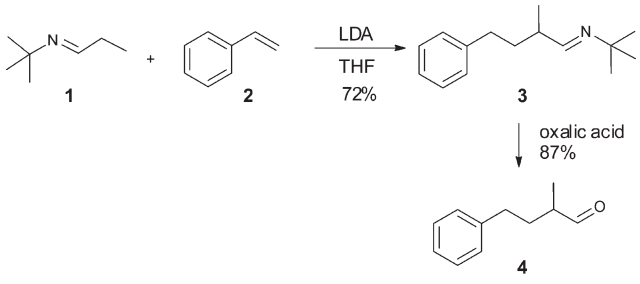
The vinylimidazole **11** was then selected as a heterocyclic equivalent of styrene and subjected to the carbolithiation with the aldimine **1**. In this case product **17** was obtained in high yield. Apparently the reaction proceeds via the addition of the vinylimidazole anion to the aldimine in a manner described in the LDA-mediated reaction of methylimidazole with propionaldehyde.[15] The pKa of methylimidazole,[16] being approximately 10 times larger than that of aldimines and ketimines,[17] can be used to explain this preferred addition mode.

A possible mechanism for the reaction of LDA-promoted styrene and aldimines is shown in Scheme 2.

Lithium-assisted ene processes are well known to occur in organic reactions.[18,19] The addition of styrene to the aldimine anion is facilitated via the chelated species **A**. The ene reaction gives the lithiated intermediate **B**, and eventually affords the product after acidic hydrolysis. In the case of R=H (aldimine **5**, entry 1, Table 1), a Li–H exchange between the intermediate **B** and diisopropylamine occurs. The resulting aldimine, an equivalent of the aldimine **1**, reacts with styrene to give the double addition product **12**.

Subsequently, the unsaturated aldimines **18**, **19** and **20** were reacted with styrene. The results are shown in Table 2.

The cyclised products *cis*-**21** and *trans*-**22** were obtained in a ratio of 1.2:1 when the α,β-unsaturated aldimine **18** was used. The stereochemistries of **21** and **22** were determined by comparison of the ^{1}H NMR coupling constants between H-1



Scheme 1 The addition of lithium *tert*-butylpropylaldimine to styrene and subsequent hydrolysis.

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Table 1 Products from carbolithiation of styrenes with simple aldimines

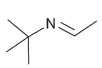
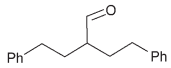
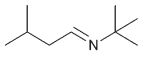
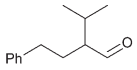
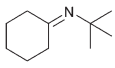
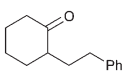
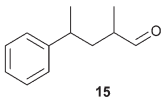
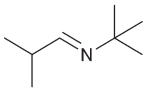
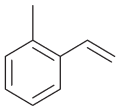
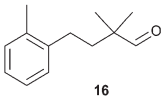
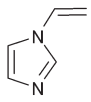
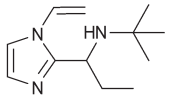
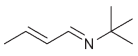
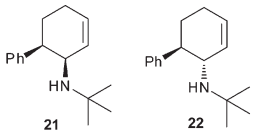
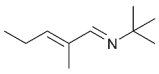
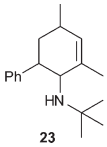
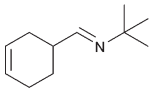
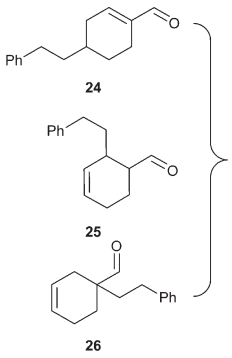
Entry	Aldimine	Styrene	Product	Yield
1	 5	2	 12	65%
2	 6	2	 13	40%
3	 7	2	 14	35%
4	1	 9	 15	30%
5	 8	 10	 16	70%
6	1	 11	 17	95%

Table 2 Products from carbolithiation of styrene with unsaturated aldimines

Entry	Aldimine	Product	Yield
1	 18	 21 22	47%
2	 19	 23	45%
3	 20	 24 25 26	36%

Conclusion

In conclusion, a simple and straightforward way to prepare 4-phenyl substituted butanals has been established *via* carbolithiation of a styrene with an LDA-mediated aldimine. It can be envisaged as a procedure for C_2-elongation. Based on this approach, derivatives of 4-phenylbutanal and 3-amine-substituted 4-phenylcyclohex-1-ene can be readily prepared from the approach with saturated and unsaturated aldimine anions.

Experimental

IR spectra were recorded with a Bruker Tensor 27 instrument. ^{1}H NMR and ^{13}C NMR spectra were recorded with Bruker AW 300 or DPX 400 instruments in $CDCl_3$. Chemical shifts are reported in δ (ppm) relative to Me_4Si (TMS). GC-MS spectroscopic data were obtained from Agilent 6890 N and MSD 5975 instruments using a HP-5 MS column. HRMS were obtained with a Bruker Microtoff 11 machine using an ESI source. Column chromatography was performed on silica gel (200–300 mesh) from the Qingdao Ocean Chemical Factory. All solvents and commercially available chemicals were used as received.

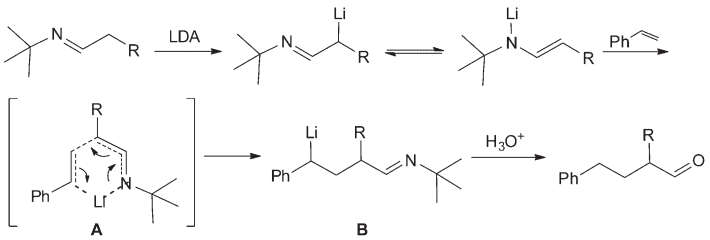
N-tert-butylaldimines **1**,[22] **5**,[23] **6**,[24] **7**,[25] **8**,[26] **18**,[27] **19**[28] and **20**[26] were prepared from the corresponding aldehyde and *tert*-butylamine according to literature methods.

Reactions of aldimines and styrenes; general procedure:
The LDA solution was prepared separately by the addition of BuLi (1.6 M, 19.0 mL, 30.0 mmol) to a solution of diisopropylamine (2.8 g,

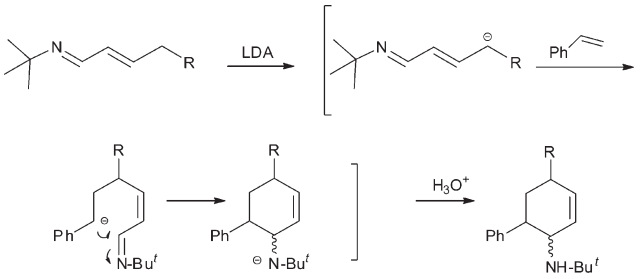
and H-2. These are 4.8 Hz at 3.04 ppm for **21** and 7.8 Hz at 3.20 ppm for **22**. The larger coupling constant for **22** results from the *trans*-coupling between H-1 and H-6 in the pseudo chair configuration.[20,21] The reaction of unsaturated aldimine **19** with styrene afforded cyclic amine **23** as a mixture of isomers in a ratio of 6.2:1. NMR analysis confirmed the *trans*-isomer to be the major product. Three addition products **24**, **25** and **26** in a ratio of 1.2:1:1 were obtained when the reaction was carried out with unsaturated aldimine **20**. Compound **24** was isolated and identified by H–H COSY and C–H COSY. The ^{13}C NMR δ of **24** at 194.2 ppm indicates that there is conjugation between the aldehydic carbon and the ring double bond in contrast to the non-conjugated counterparts **25** and **26** in which the corresponding chemical shifts are 205.6 and 204.5 ppm respectively. The ^{13}C NMR showed the chemical shifts of C-2 for **25** and **26** to be 51.0 and 48.2 respectively. Hence these two isomers **25** and **26** were assigned as shown in Table 2 based on NMR analysis.

The regioselectivity and the stereochemistry of cyclic products in the Table 2 can be explained by the mechanism as shown in Scheme 3.

Apparently the internal double bond migration occurred in the lithiation stage and consequently, the addition of styrene to the anions at different positions afforded **24**, **25** and **26** as shown in Scheme 4.



Scheme 2 A possible mechanism for LDA-promoted reaction of styrene and aldimines.



Scheme 3 A possible mechanism for the formation of the cyclic amines.

27.9 mmol) in THF (20 mL) with stirring at –78 °C under argon. The resulting solution was warmed to RT and stirred for 20 min. It was then added dropwise to a solution of **1** (3.0 g, 26.5 mmol) and styrene (2.5 g, 24.0 mmol) in THF (30 mL) with stirring at –78 °C under argon. The reaction mixture was warmed gradually to RT and stirred for 8 h. The reaction was quenched with water (50 mL) at 0 °C. The organic phase was separated and the aqueous phase was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were washed with saturated sodium bicarbonate (20 mL), dried over $MgSO_4$. The solvent was removed by rotary evaporation, and the remaining oil was distilled under reduced pressure to give 2-methyl-*N*-(2-methyl-4-phenylbutylidene)propan-2-amine **3** as a light yellow oil, b.p., 140 °C/1.5^{-1} mbar; IR (film, ν, cm^{-1}) 1671 (C=N), 1453, 1364. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.38 (d, J = 6.6 Hz, 1H, H-1), 7.14–7.30 (m, 5H, Ph), 2.51–2.64 (m, 2H, H-4), 2.31–2.42 (m, 1H, H-2), 1.60–1.85 (m, 2H, H-3), 1.17 (s, 9H, 3 × Me), 1.08 (d, J = 6.8 Hz, 3H, 2-Me). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 163.0 (C-1), 142.4, 128.4, 128.3 and 125.7 (Ar C), 56.4 (*tert*-C), 39.7 (C-2), 36.3 (C-4), 33.5 (C-3), 29.7 (3 × Me), 17.8 (2-Me); MS *m/z* (%) 217 (M$^+$, 1), 202 (4), 175 (1), 160 (2), 145 (11), 126 (8), 113 (100), 98 (78); HRMS: calcd for $C_{15}H_{23}N$[M + H$^+$] 218.1903; found: 218.1903.

2-Methy-4-phenylbutanal (**4**): The same procedure was applied as described for **3** except the quench stage was performed with sat. NH_4Cl solution (50 mL). Oxalic acid (*ca* 5–8 g) was added portion-wise until the aqueous phase had reached pH 3–4. The resulting mixture was stirred at RT for 3 h. Work-up as described above and further purification by column chromatography afforded **4**,[29–32] b.p. 95–97 °C/1.5^{-1} mbar. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.62 (*J* 1.8 Hz, 1H, H-1), 7.15–7.30 (m, 5H, Ph), 2.58–2.72 (m, 2H, H-4), 2.30–2.44 (m, 1H, H-2), 1.99–2.13 (m, 1H, H-3^A), 1.60–1.74 (m, 1H, H-3^B), 1.15 (d, J = 7.0 Hz, 3H, 2-Me). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 204.8 (C-1), 141.4, 128.5, 128.4(9) and 126.1 (Ar C), 45.6 (C-2), 33.1 (C-4), 32.2 (C-3), 13.4 (2-Me). MS *m/z* (%) 162 (M$^+$, 5), 144 (2), 128 (2), 104 (100), 91 (48). The analytical and spectroscopic data of the other products obtained by the same procedure are given below.

2-Phenethyl-4-phenylbutanal (**12**): Oil, IR (film, ν, cm^{-1}) 1720 (C=O), 1602, 1495, 1454. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.60 (d, J = 2.5 Hz, 1H, C*H*O), 7.13–7.30 (m, 10H, Ph), 2.53–2.69 (m, 4H, 2 × CH_2), 2.32–2.37 (m, 1H, C*H*), 1.95–2.07 (m, 2H, CH_2), 1.72–1.84 (m, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 204.5 (C-1), 141.3, 128.5, 128.4 and 126.1 (Ar C), 50.6 (C-2), 33.2 (*C*H$_2$), 30.5 (*C*H$_2$); MS *m/z* (%) 252 (M$^+$, 1), 234 (4), 148 (22), 130 (15), 104 (55), 92 (100), 90 (75), 77 (7); HRMS: calcd for $C_{18}H_{20}O$[M + H$^+$] 253.1587; found: 253.1586.

2-Isopropyl-4-phenylbutanal (**13**),[33] oil, ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.67 (d, J = 3.0 Hz, 1H, C*H*O), 7.15–7.30 (m, 5H, Ph), 2.61–2.72 (m, 1H, H^A-3), 2.43–2.58 (m, 1H, H^B-3), 2.09–2.19 (m, 1H, H-2), 1.91–2.09 (m, 2H, H-4), 1.68–1.81 (m, 1H, C*H*), 0.96 (d, J = 6.7 Hz, 3H, CH_3), 0.95 (d, J = 6.7 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 205.5 (*C*HO), 141.7, 128.4(3), 128.3(8) and 126.0 (Ar C), 57.6 (C-2), 33.8 (C-4), 28.3 (*C*H), 27.7 (C-3), 20.1 (Me), 19.6 (Me); MS *m/z* (%) 190 (M$^+$, 2), 129 (2), 115 (2), 104 (100), 91 (48), 71 (22).

2-Phenethylcyclohexanone (**14**):[34] Oil, IR (film, ν, cm^{-1}) 1721 (C=O). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.18–7.32 (m, 5H, Ph), 2.62 (t, J = 7.8 Hz, 2H, CH_2), 1.95–2.45 (m, 6H, 3 × CH_2), 1.31–1.90 (m, 5H, CH and 2 × CH_2); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 213.1 (C=O), 142.2, 128.4, 128.3, 125.8, 49.9 (*C*H), 42.1, 34.1, 33.2, 31.2, 28.1, 24.9; MS *m/z* (%) 202 (M$^+$, 5), 115 (2), 104 (6), 98 (100), 83 (16), 70 (17).

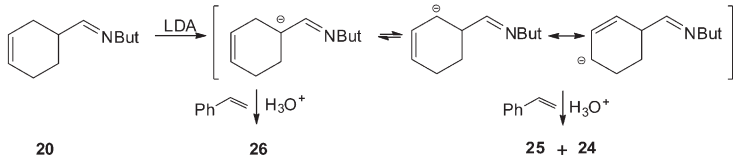
2-Methyl-4-phenylpentanal (**15** *as two diastereoisomers*): Oil, IR (film, ν, cm^{-1}) 1722 (C=O), 1494, 1453. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.57 and 9.48 (two s, 1 H, C*H*O), 7.14–7.33 (m, 5H, Ph), 2.72–2.83 (m, 1H, H-4), 1.93–2.32 (m, 2H, H^A-3 and H-2), 1.44–1.66 (m, 1H, H^B-3), 1.28 and 1.26 (two d, J = 7.7 Hz, 3H, 4-Me), 1.07 and 1.05 (two d, J = 6.8 Hz, 3H, 2-Me); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 204.9(1) and 204.8(5), 146.4 and 145.9, 128.6(2) and 128.5(7), 127.0, 126.4 and 126.3 (Ar C), 44.5 and 44.4 (C-2), 39.4 and 38.6 (C-3), 37.5 and 37.3 (C-4), 23.0 and 22.4 (4-Me), 14.1 and 13.2 (2-Me); MS *m/z* (%) 176 (M$^+$, 2), 143 (1), 128 (1), 118 (100), 105 (65), 91 (20); HRMS: Calcd for $C_{12}H_{16}O$[M + H$^+$] 177.1274, Found: 177.1279.

2,2-Dimethyl-4-(o-tolyl)butanal (**16**): IR (film, ν, cm^{-1}) 1720 (C=O), 1460. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.52 (s, 1H, C*H*O), 7.09–7.14 (m, 4H, Ph), 2.46–2.57 (m, 2H, CH_2), 2.29 (s, 3H, CH_3), 1.68–1.77 (m, 2H, CH_2), 1.15 (s, 6H, 2 × Me). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 205.9, 140.0, 135.7, 130.3, 128.7, 126.2, 126.1 (Ar C), 45.9 (C-2), 38.0 (C-4), 28.1 (C-3), 21.3 (2 × Me), 19.1 (Me); MS *m/z* (%) 190 (M$^+$, 5), 172 (1), 157 (1), 145 (1), 129 (2), 119 (53), 118 (52), 105 (100); HRMS: calcd for $C_{13}H_{18}O$[M + H$^+$] 191.1430; found: 191.1428.

N-(tert-butyl)-1-(1-vinyl-1H-imidazol-2-yl)propan-1-amine (**17**): IR (film, ν, cm^{-1}) 1644, 1484. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.59 (dd, J = 15.8 and 8.8 Hz, 1H, CH_2=C*H*), 7.13 (d, J = 1.2 Hz, 1H, =C*H*N=), 6.95 (d, J = 0.9 Hz, 1H, =C*H*N), 5.15 (dd, J = 15.8 and 1.2 Hz, 1H, =C*H*^{A}H), 4.82 (dd, J = 8.8 and 1.2 Hz, 1H, =C*H*^{B}H), 3.96 (t, J = 7.2 Hz, 1H, C*H*), 1.57–1.78 (m, 2H, CH_2), 0.97 (s, 9H, 3 × Me), 0.85 (t, J = 7.5 Hz, 3H, Me); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 151.1, 129.8, 128.0, 115.4, 101.0, 52.9, 50.9 (*tert*-C), 30.8, 29.5 (3 × Me), 10.8; MS *m/z* (%) 207 (M$^+$, 0.5), 192 (6), 178 (93), 150(1), 135 (88), 122 (100), 107 (5), 95 (15); HRMS: calcd for $C_{12}H_{21}N_3$[M + H$^+$] 208.1808; found: 208.1805.

Syn- and anti-N-(tert-butyl)-1,2,5,6-tetrahydro-[1,1-biphenyl]-2-amine (**21** and **22**) *as a mixture*: ^{1}H NMR ($CDCl_3$, 400 MHz): **21** δ 7.15–7.22 (m, 5H, Ph), 5.86–5.92 (m, 1H, H-3), 5.58–5.63 (m, 1H, H-4), 3.04 (t, J = 4.8 Hz, 1H, H-2), 2.71–2.75 (m, 1H, H-1), 1.95–1.99 (m, 2H, CH_2), 1.85–1.90 (m, 2H, CH_2), 0.68 (s, 9H, 3 × Me); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.3, 128.5, 128.2, 128.0 (Ar C), 133.3 (C-3), 126.0 (C-4), 50.2 (*tert*-C), 48.1 (C-2), 46.5 (C-1), 30.3 (3 × Me), 24.9 (C-6), 23.3 (C-5); **22** δ 7.13–7.23 (m, 5H, Ph), 5.79 (app. dq, J = 10.0 and 2.1 Hz, 1H, H-3), 5.62–5.68 (m, 1H, H-4), 3.20 (dt, J = 7.8 and 2.1 Hz, 1H, H-2), 2.53 (ddd, J = 10.2, 7.8 and 3.4 Hz, 1H, H-1), 1.82–1.94 (m, 4H, H-5, 6), 0.81 (s, 9H, 3 × Me); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.7, 128.2, 127.9, 127.6 (Ar C), 134.1 (C-3), 126.5 (C-4), 53.8 (C-2), 50.6 (*tert*-C), 49.3 (C-1), 29.7 (3 × Me), 28.9 (C-6), 24.9 (C-5); MS *m/z* (%) 229 (M$^+$, 1), 214 (1), 171 (1), 157 (2), 141 (1), 125 (100), 110 (11), 91 (17); HRMS: calcd for $C_{16}H_{23}N$[M + H$^+$] 230.1903; found: 230.1903.

N-(tert-butyl)-3,5-dimethyl-1,2,5,6-tetrahydro-[1,1-biphenyl]-2-amine (**23**): Oil, ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.19–7.26 (m, 5H, Ph), 5.29 (brs, 1H, H-4), 2.96–3.06 (m, 1H, H-2), 2.78 (app. dt, J = 12.1 and 3.1 Hz, 1H, H-1), 2.17–2.25 (m, 1H, H-5), 1.88 (s, 3H, 3-Me), 1.60–1.75 (m, 2H, H-6), 1.04 (d, J = 7.0 Hz, 3H, 5-Me), 0.57 (s, 9H, 3 × Me); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 145.5, 129.4, 127.5 and 125.8 (Ar C), 137.4 (C-3), 130.4 (C-4), 55.0 (C-2), 49.9 (*tert*-C), 46.9 (C-1), 32.5 (C-5), 31.3 (C-6), 30.2 (3 × Me), 23.3 (Me), 21.9 (Me); MS *m/z* (%) 257 (M$^+$, 1), 215 (2), 169 (3), 153 (100), 138 (16), 97 (48), 82 (14); HRMS: calcd for $C_{18}H_{27}N$[M + H$^+$]258.2216; found: 258.2216.



Scheme 4 Double bond migration in the reaction of **20** and styrene.

4-Phenethylcyclohex-1-enecarbaldehyde (**24**): Oil, IR (film, ν, cm^{-1}) 1680 (C=O), 1642, 1495, 1453. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.42 (s, 1H, C*H*O), 7.16–7.31 (m, 5H, Ph), 6.78 (m, 1H, H-2), 2,71 (t, J = 7.8 Hz, 2H, PhCH_2), 2.35–2.58 (m, 2H, CH_2), 1.83–2.15 (m, 3H, CH and CH_2), 1.58–1.71 (m, 3H, CH_2 and H-5^A), 1.19–1.37 (m, 1H, H-5^B). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 194.1(CHO), 150.7(C-2), 142.3, 141.6, 128.4, 128.3, 125.8, 37.9, 33.2, 33.0, 32.9 (C-4), 27.5, 21.1; MS *m/z* (%) 214 (M^+, 34), 196 (4), 181 (3), 167 (2), 143 (11), 122 (13), 109 (37), 91 (100); HRMS: calcd for $C_{15}H_{18}O$[M + H^+]215.1430; found: 215.1430.

2-Phenethylcyclohex-3-enecarbaldehyde (**25**) *and 1-Phenethylcyclohex-3-enecarbaldehyde* (**26**): Oil, IR (film, ν, cm^{-1}) were obtained as a mixture from silica gel chromatography. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.62 and 9.50 (two s, 1H, C*H*O), 7.08–7.35 (m, 5H, Ph), 5.73 and 5.69 (two brs, 2H, olefinic), 2.24–2.85 (m, 4H, PhCH_2CH_2), 1.53–2.18 (m, 6H, ring CH_2 and C*H*); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 205.6 and 204.5 (*C*HO), 142.0 and 141.9 (Ar C), 129.0, 128.5, 128.4, 128.3, 128.2, 127.1, 126.9, 126.0, 125.9 and 124.4 (Ar C and *C*H=*C*H), 51.0 (C-1 of **25**), 48.2 (C-1 of **26**), 37.7 and 36.5 (*C*H_2), 33.8 (C-2 of **25**), 33.0, (C-2 of **26**), 30.2, 29.8, 27.4, 23.3, 22.3 and 21.0 (*C*H_2); MS *m/z* (%) 214 (M^+, 11), 196 (19), 185 (9), 168 (3), 143 (3), 129 (5), 117 (10), 105 (42), 91 (100); HRMS: calcd for $C_{15}H_{18}O$ [M + H^+] 215.1430; found: 215.1430.

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