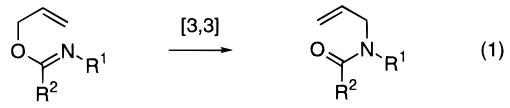
# Allylic Transposition of Alcohol and Amine Functionality by Thermal or Palladium(II)-Catalyzed Rearrangements of Allylic *N*-Benzoylbenzimidates

Larry E. Overman* and G. Greg Zipp

*Department of Chemistry, 516 Physical Sciences 1, University of California, Irvine, California 92697-2025*

*Received November 13, 1996*

The 1,3 rearrangement of allylic imidates to allylic amides allows readily available allylic alcohols to serve as precursors of less accessible allylic amides and amines. Especially widely used is the rearrangement of allylic trichloroacetimidates to allylic trichloroacetamides, which was introduced by one of us in 1974 (eq 1, $R^1 = H$, $R^2 = CCl_3$).[1] During the course of our current studies to develop asymmetric catalysts for allylic imidate rearrangements,[2] we became interested in the related rearrangement of allylic *N*-benzoylbenzimidates to allylic dibenzamides (eq 1, $R^1 = Bz$, $R^2 = Ph$). Similar to allylic trichloroacetimidates, allylic *N*-benzoylbenzimidates should be available from allylic alcohol starting materials under mild, nonacidic conditions.[3] Allylic *N*-benzoylbenzimidates would differ from allylic trichloroacetimidates in their much reduced basicity, which could allow a wider variety of metals to catalyze their rearrangement to allylic dibenzamides.[4,5]



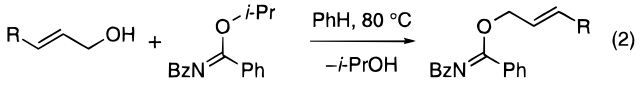

**1** **2** (1)

In this Note we report that allylic *N*-benzoylbenzimidates can be made from a variety of primary and secondary allylic alcohols by either Mitsunobu displacement or imidate exchange, and that these intermediates undergo efficient [3,3]-sigmatropic rearrangement to allylic dibenzamides in the presence of $PdCl_2(MeCN)_2$ at room temperature or thermally at elevated temperatures.

## Results and Discussion

**Preparation of *N*-Benzoylbenzimidates**. Secondary allylic alcohols undergo clean *O*-alkylation with dibenzamide[6] under the Mitsunobu conditions described by Sammes[3c] to form allylic *N*-benzoylbenzimidates in good yield. In the representative examples summarized in entries 1−4 of Table 1, less than 4% of *N*-alkylation was observed and $S_N2'$ products were not detected. The *N*-benzoylbenzimidate intermediates were conveniently purified by simple flash chromatography on silica gel.

In contrast, Mitsunobu reaction of *trans*-2-hexen-1-ol with dibenzamide was not clean and provided a 2.5:1 mixture of *O*- and *N*-alkylated products. Numerous attempts to improve this ratio by modifications of various reaction parameters were unsuccessful. As a result, primary allylic alcohols were converted to *N*-benzoylbenzimidate derivatives through imidate exchange with 2-propyl *N*-benzoylbenzimidate (**11**, eq 2).[7] This exchange reaction was most conveniently accomplished by slowly concentrating (distillation at atmospheric pressure using a simple Vigreux column) a benzene solution of the primary allylic alcohol and 1.0 equiv of **11**. Final purification by flash chromatography on silica gel gave the benzoylbenzimidate products in 81−86% yield (entries 5−8, Table 1).




**11** (2)

**Palladium (II)-Catalyzed Rearrangements**. Exposure of primary *N*-benzoylbenzimidates **7**−**9** to 5 mol % $PdCl_2(MeCN)_2$ in $CH_2Cl_2$ at rt occasioned rearrangement to the corresponding allylically transposed dibenzamides **16**−**18**. However, secondary *N*-benzoylbenzimidates rearranged less efficiently under these conditions. The problem was traced to competing elimination, which was signaled by the isolation of dibenzamide. The simple expedient of decreasing the solvent polarity to toluene reduced this competing process to acceptable levels. Using toluene as the solvent, *N*-benzoylbenzimidates **3**−**9** rearranged at rt in the presence of 5% $PdCl_2(MeCN)_2$ to provide dibenzamides **12**−**18** in 86−92% yield. The allylic dibenzamide products showed five diagnostic signals in the $^{13}C$ NMR spectra for the two equivalent benzoyl groups. The geraniol-derived benzoylbenzimidate **10** was not converted in high yield to linalyl imide **19** under similar conditions. This latter reaction was slow and produced up to 35% of geranyl dibenzamide, the product of 1,3-rearrangement. Since the rearrangement of 3-methyl-2-butenyl benzimidate **9** to imide **18** took place efficiently (entry 7, Table 1), the distal double bond of **10** is presumably the cause of the lower yield of the $PdCl_2$-catalyzed rearrangement of the geranyl substrate.

Stereoselectivity in forming disubstituted alkene products was extremely high, since only the *E* isomer of **12** or **13** could be detected by $^{13}C$ NMR analysis of the crude rearrangement product. To quantify stereoselection in the rearrangement of **5** to trisubstituted imide **14**, the *Z* stereoisomer of **14** was prepared as outlined in Scheme 1. Capillary GLC analysis then established that diastereoselectivity in the $PdCl_2$-catalyzed conversion of **5** → **14** was 98:2.

**Thermal Rearrangements**. The rearrangement of a representative group of allylic *N*-benzoylbenzimidates under thermal conditions was also examined. Refluxing xylenes (bp 137−144 °C) was required, and yields were significantly lower than for the $PdCl_2$-catalyzed re-

(1) (a) Overman, L. E. *J. Am. Chem. Soc.* **1974**, *96*, 597. (b) Overman, L. E. *J. Am. Chem. Soc.* **1976**, *98*, 2901. (c) Overman, L. E. *Acc. Chem. Res.* **1980**, *13*, 218.

(2) Calter, M.; Hollis, K. T.; Overman, L. E.; Ziller, J.; Zipp, G. G. *J. Org. Chem.* **1997**, *62*, 1449.

(3) (a) Mitsunobu, O.; Wada, M.; Sano, T. *J. Am. Chem. Soc.* **1972**, *94*, 679. (b) Wada, M.; Sano,T.; Mitsunobu, O. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2833. (c) Sammes, P. G.; Thetford, D. *J. Chem. Soc., Perkin Trans. 1* **1988**, 111.

(4) Mercury(II) salts[1] and palladium(II) complexes[1c,5] have been employed most widely to catalyze the rearrangement of allylic imidates.

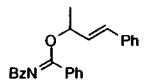
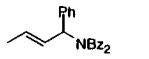
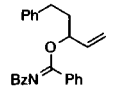
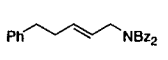
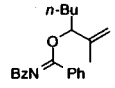
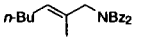
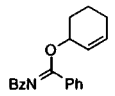
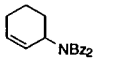
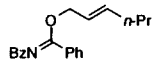
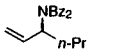
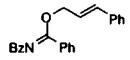
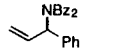
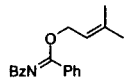
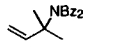
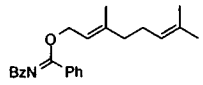
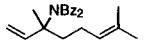
(5) (a) Ikariya, T.; Ishikawa, Y.; Yoshikawa, S. *Chem. Lett.* **1982**, 1815. (b) Schenck, T. G.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107*, 2058. (c) Metz, P.; Mues, C.; Schoop, A. *Tetrahedron* **1992**, *48*, 1071. (d) Mehmandoust, M.; Petit, Y.; Larchevêque, M. *Tetrahedron Lett.* **1992**, *33*, 4313.

(6) Titherley, A. W. *J. Chem. Soc.* **1904**, 1673.

(7) Exchange reactions have been employed previously to prepare simple imidates, see, e.g.: Roberts, R. M.; Higgins, T. D., Jr.; Noyes, P. R. *J. Am. Chem. Soc.* **1955**, *77*, 3801.

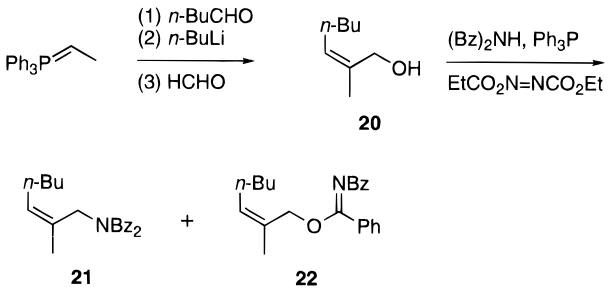
S0022-3263(96)02129-9 CCC: $14.00 

**Table 1. Preparation of Allylically Rearranged Dibenzamides from Allylic Alcohols**

| | Allylic *N*-Benzoylbenzimidate | | | | Allylic Dibenzamide | | |
|---|---|---|---|---|---|---|---|
| entry | | compd | method[a] | yield, % | compd | $PdCl_2$-catalyzed[b] Yield, % | Thermal[c] Yield, % |
| 1 |  | **3** | A | 76 |  | **12** | 86[d] | 63[d] |
| 2 |  | **4** | A | 84 |  | **13** | 91[d] | 62[d] |
| 3 |  | **5** | A | 86 |  | **14** | 92[e] | 54[e] |
| 4 |  | **6** | A | 93 |  | **15** | 87 | nd |
| 5 |  | **7** | B | 83 |  | **16** | 90 | nd |
| 6 |  | **8** | B | 81 |  | **17** | 91 | nd |
| 7 |  | **9** | B | 86 |  | **18** | 89 | nd |
| 8 |  | **10** | B | 84 |  | **19** | 50 | 60 |

[a] Method A: $Bz_2NH$, DEAD, $Ph_3P$, THF, rt; Method B: **11** (1.0 equiv), 80 °C, remove *i*-PrOH by distillation. [b] 5% $PdCl_2(MeCN)_2$, toluene, rt. [c] Xylenes, reflux. [d] Single stereoisomer by $^1H$ and $^{13}C$ NMR analysis. [e] Isomer ratios were determined by capillary GLC analysis: 98.0% *E* ($PdCl_2$-catalyzed); 98.1% (thermal).

**Scheme 1**




arrangement (Table 1). The one exception was geranyl imidate **10**, which gave the corresponding linalyl imide **19** in slightly higher yield under thermal conditions. Stereoselection was also high in the thermal rearrangements with **14** being formed as a 98:2 mixture of *E* and *Z* stereoisomers.

**Conclusion**. The [3,3]-sigmatropic rearrangement of allylic *N*-acylimidates to allylic imides has been demonstrated for the first time. In the presence of 5% $PdCl_2(MeCN)_2$ the rearrangement of allylic *N*-benzoylbenzimidates takes place in high yield within hours at rt. Since the preparation of allylic *N*-benzoylbenzimidates and their 1,3 transposition to allylic dibenzamides can be accomplished under mild, neutral conditions, this sequence for 1,3-transposition of oxygen and nitrogen functionality should find application in the synthesis of nitrogen-containing materials.

## Experimental Section[8-10]

**General Procedure for Preparing *N*-Benzoylbenzimidates by Mitsunobu Reaction. 4-Phenylbut-3-en-2-yl *N*-Benzoylbenzimidate (3).** Following the general procedure

(8) General experimental details: All reactions were carried out under an atmosphere of Ar or $N_2$, and concentrations were performed under reduced pressure using a Büchi rotary evaporator. Tetrahydrofuran (THF), $Et_2O$ and $CH_2Cl_2$ were degassed with Ar then passed through two 4 × 36 in columns of anhydrous neutral A-2 alumina (8 × 14 mesh; LaRoche Chemicals; activated under a flow of Ar at 350 °C for 3 h) to remove water.[9] Toluene was degassed with Ar, and then passed through a 4 × 36 in column of anhydrous neutral A-2 alumina (8 × 14 mesh; LaRoche Chemicals; activated under a flow of Ar at 350 °C for 3 h) to remove water and then through a 4 × 36 in column of Q-5 reactant (Englehard; activated under a flow of 5% $H_2/N_2$ at 250 °C for 3 h) to remove $O_2$.[9] NMR spectra were measured on a Bruker AC300 FT NMR spectrometer or General Electric GN500 FT NMR spectrometer. $^1H$ NMR chemical shifts are reported as $\delta$ values in ppm, coupling constants are reported in hertz and refer to apparent multiplicities. Multiplicity is indicated as follows: s (singlet); d (doublet); t (triplet); m (multiplet); app t (apparent t); dd (doublet of doublets), etc. High resolution mass spectra were measured on a MicroMass Analytical 7070E (EI or CI-isobutane), uncertainty ($\sigma$) in mass measurments is 1.0 millimass unit (molecular weight < 400) or 1.5 millimass units (molecular weight 400−1000). FAB mass spectra were measured with a MicroMass AutoSpec E spectrometer. Infrared spectra were recorded using a Perkin Elmer 1600 FTIR spectrometer. Microanalyses were performed by Atlantic Microlabs, Atlanta, GA. TLC and column chromatography were performed as described by Still[10] using E. Merck silica gel (43-60 $\mu$m) with a loading of approximately 30:1 $SiO_2$−substrate. Analytical GLC analyses were performed on a Hewlet Packard 5890 Series II with a 30 m × 0.32 mm Supelco SPB-1 column.

(9) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

(10) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

of Sammes,[3c] diethyl azodicarboxylate (0.77 mL, 4.9 mmol) was added dropwise to a precooled (0 °C) solution of dibenzamide (1.0 g, 4.4 mmol), $Ph_3P$ (1.3 g, 4.9 mmol), 4-phenyl-3-buten-2-ol (0.66 g, 4.4 mmol), and THF (20 mL). The resulting mixture was maintained for 1 h at 0 °C and then allowed to warm to rt. After 2 h, the reaction was concentrated, and the residue was purified by flash chromatography (20:1 hexane−EtOAc) to afford 1.2 g (76%) of **3** as a colorless oil that was homogeneous by TLC analysis:[11] $R_f$ 0.22 (9:1 hexane−EtOAc); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.99 (d, $J$ = 8.0 Hz, 2H), 7.61 (d, $J$ = 7.3 Hz, 2H), 7.47 (t, $J$ = 7.3 Hz, 2H), 7.43−7.23 (m, 8H), 7.12 (t, $J$ = 7.7 Hz, 1H), 6.77 (d, $J$ = 16.0 Hz, 1H), 6.38 (dd, $J$ = 16.0, 7.0 Hz, 1H), 5.83 (quin, $J$ = 6.6 Hz, 1H), 1.64 (d, $J$ = 6.4 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) 175.7, 173.4, 157.4, 136.1, 134.0, 132.4, 131.6, 131.4, 130.5, 129.9, 129.3, 128.5, 128.3, 127.8, 127.2, 126.4, 74.1, 20.5 ppm; IR (film) 1657, 1651, 1599 cm$^{-1}$; MS (EI) $m/z$ 355.1559 (355.1572 calcd for $C_{24}H_{21}NO_2$).

**5-Phenyl-1-penten-3-yl *N*-Benzoylbenzimidate (4)**. A colorless oil that was homogeneous by TLC analysis:[11] $R_f$ 0.21 (9:1 hexane−EtOAc); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.97 (d, $J$ = 7.2 Hz, 2H), 7.59 (d, $J$ = 9.6 Hz, 2H), 7.54 (t, $J$ = 8.0 Hz, 1H), 7.45−7.41 (m, 3H), 7.35−7.30 (m, 4H), 7.25−7.21 (m, 3H), 6.02 (ddd, $J$ = 17.2, 10.5, 6.4 Hz, 1H), 5.58 (q, $J$ = 6.4 Hz, 1H), 5.43 (d, $J$ = 17.2 Hz, 1H), 5.36 (d, $J$ = 10.5 Hz, 1H), 2.92−2.73 (m, 2H), 2.34−2.25 (m, 1H), 2.18−2.13 (m, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) 175.7, 157.5, 141.2, 136.2, 134.2, 132.6, 131.6, 130.6, 129.5, 128.6, 128.5, 128.4, 126.0, 117.6, 35.9, 31.4 ppm (one carbon, presumed buried under $CDCl_3$, is not observed); IR (film) 1658, 1651, 1600 cm$^{-1}$; MS (CI) $m/z$ 370.1799 (370.1807 calcd for $C_{25}H_{24}NO_2$).

**6-Methyl-1-hepten-3-yl *N*-Benzoylbenzimidate (5)**. A colorless oil that was homogeneous by TLC analysis:[11] $R_f$ 0.19 (9:1 hexane−EtOAc); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.98 (d, $J$ = 7.5 Hz, 2H), 7.60 (d, $J$ = 7.5 Hz, 2H), 7.52 (t, $J$ = 7.4 Hz, 1H), 7.43−7.38 (m, 3H), 7.31 (t, $J$ = 7.4, 2H), 5.43 (t, $J$ = 6.5, 1H), 5.11 (s, 1H), 5.04 (s, 1H), 1.95−1.88 (m, 1H), 1.86 (s, 3H), 1.83−1.81 (m, 1H), 1.47−1.39 (m, 4H), 0.95 (t, $J$ = 6.8, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) 175.6, 157.2, 143.3, 134.2, 132.4, 131.5, 130.7, 129.3, 128.3, 128.2, 128.0, 112.8, 80.5, 32.5, 27.5, 22.5, 18.2, 13.8 ppm; IR (film) 1697, 1654, 1600 cm$^{-1}$; MS (CI) $m/z$ 336.1952 (336.1963 calcd for $C_{22}H_{26}NO_2$).

**2-Cyclohexenyl *N*-Benzoylbenzimidate (6)**. A colorless oil that was homogeneous by TLC analysis: $R_f$ 0.18 (9:1 hexane−EtOAc); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.02 (d, $J$ = 8.2 Hz, 2H), 7.58 (d, $J$ = 8.7 Hz, 2H), 7.54 (t, $J$ = 6.8 Hz, 1H), 7.45 (t, $J$ = 6.2 Hz, 2H), 7.40 (t, $J$ = 7.5 Hz, 1H), 7.29 (t, $J$ = 6.3 Hz, 2H), 6.11−5.98 (m, 2H), 5.62−5.55 (m, 1H), 2.24−2.03 (m, 4H), 1.91−1.83 (m, 1H), 1.77−1.69 (m, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) 175.9, 158.4, 134.4, 133.2, 132.7, 131.5, 130.8, 129.4, 128.6, 128.5, 125.3, 71.2, 28.2, 25.0, 18.9 ppm; IR (film) 1672, 1653, 1599 cm$^{-1}$; MS (CI) $m/z$ 306.1486 (306.1494 calcd for $C_{20}H_{20}NO_2$). Anal. Calcd for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.41; H, 6.32; N, 4.47.

**Isopropyl *N*-Benzoylbenzimidate (11)**. A colorless oil that was homogeneous by TLC analysis:[11] $R_f$ 0.20 (9:1 hexane−EtOAc); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.01 (d, $J$ = 8.5 Hz, 2H), 7.60−7.47 (m, 3H), 7.47−7.34 (m, 3H), 7.30 (t, $J$ = 7.0 Hz, 2H), 5.33 (heptet, $J$ = 6.2 Hz, 1H), 1.48 (d, $J$ = 6.2 Hz, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$) 175.9, 158.6, 132.6, 131.4, 130.9, 129.4, 128.4, 71.0, 21.8 ppm; IR (film) 1652, 1600 cm$^{-1}$; MS (CI) $m/z$ 268.1331(268.1337 calcd for $C_{17}H_{18}NO_2$).

**General Procedure for Forming *N*-Benzoylbenzimidates by Exchange with 11. *trans*-2-Hexenyl *N*-Benzoylbenzimidate (7)**. A solution of **11** (0.53 g, 2.0 mmol), *trans*-2-hexen-1-ol (0.24 mL, 2.0 mmol), and benzene (40.0 mL) was heated at 80 °C while the benzene/2-propanol azeotrope was collected using a Vigreux column until the total reaction volume was ∼5 mL. This solution was concentrated, and the residue was purified by flash chromatography (20:1 hexane−EtOAc) to yield 0.51 g (83%) of **7** as a colorless oil that was homogeneous by TLC analysis:[11] $R_f$ 0.19 (9:1 hexane−EtOAc); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.01 (d, $J$ = 8.2 Hz, 2H), 7.60 (d, $J$ = 5.3 Hz, 2H), 7.54 (t, $J$ = 6.3 Hz, 1H), 7.44 (t, $J$ = 7.2 Hz, 2H), 7.42 (t, $J$ = 13.6 Hz, 1H), 7.30 (t, $J$ = 7.8 Hz, 2H), 5.92 (dt, $J$ = 15.4, 6.5 Hz, 1H), 5.79 (dt, $J$ = 15.4, 6.2 Hz, 1H), 4.87 (d, $J$ = 6.1 Hz, 2H), 2.11 (q, $J$ = 7.0 Hz, 2H), 1.46 (sextet, $J$ = 7.4 Hz, 2H), 0.94 (t, $J$ = 7.4 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) 175.9, 158.2, 136.9, 134.2, 132.7, 131.6, 130.5, 129.5, 128.5, 123.8, 68.7, 34.4, 22.1, 13.7 ppm; IR (film) 1672, 1654, 1602 cm$^{-1}$; MS (CI) $m/z$ 308.1648 (308.1650 calcd for $C_{20}H_{22}NO_2$).

***trans*-Cinnamyl *N*-Benzoylbenzimidate (8)**. A colorless oil that was homogeneous by TLC analysis:[11] $R_f$ 0.15 (9:1 hexane−EtOAc); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.04 (d, $J$ = 7.2 Hz, 2H), 7.64 (d, $J$ = 7.3 Hz, 2H), 7.51 (t, $J$ = 6.1 Hz, 1H), 7.47−7.25 (m, 10H), 6.82 (d, $J$ = 15.9 Hz, 1H), 6.51 (dt, $J$ = 15.9, 6.3 Hz, 1H), 5.09 (d, $J$ = 6.3 Hz, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) 175.9, 158.1, 136.2, 134.7, 134.1, 132.9, 131.8, 130.4, 129.5, 128.7, 128.5, 128.2, 126.7, 123.1, 68.4 ppm; IR (film) 1674, 1651, 1599 cm$^{-1}$; MS (EI) $m/z$ 341.1416 (341.1416 calcd for $C_{23}H_{19}NO_2$).

**3-Methyl-2-butenyl *N*-Benzoylbenzimidate (9)**. A colorless oil that was homogeneous by TLC analysis:[11] $R_f$ 0.23 (9:1 hexane−EtOAc); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.01 (d, $J$ = 7.2 Hz, 2H), 7.60 (d, $J$ = 7.2 Hz, 2H), 7.53 (t, $J$ = 7.3 Hz, 1H), 7.43 (t, $J$ = 7.6 Hz, 2H), 7.40 (t, $J$ = 7.3 Hz, 1H), 7.30 (t, $J$ = 7.4 Hz, 2H), 5.58 (t, $J$ = 7.1 Hz, 1H), 4.91 (d, $J$ = 7.1 Hz, 2H), 1.83 (s, 3H), 1.78 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) 176.0, 158.4, 139.5, 134.2, 132.7, 131.5, 130.6, 129.4, 128.5, 128.4, 128.2, 118.5, 64.9, 25.8, 18.3 ppm; IR (film) 1675, 1651, 1600 cm$^{-1}$; MS (CI) $m/z$ 294.1474 (294.1494 calcd for $C_{19}H_{20}NO_2$).

**3,7-Dimethyl-2,6-octadienyl *N*-Benzoylbenzimidate (10)**. A colorless oil that was homogeneous by TLC analysis:[11] $R_f$ 0.24 (9:1 hexane−EtOAc); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.02 (d, $J$ = 6.9 Hz, 2H), 7.60 (d, $J$ = 9.6 Hz, 2H), 7.53 (t, $J$ = 5.9 Hz, 1H), 7.50−7.35 (m, 3H), 7.31 (d, $J$ = 6.4 Hz, 2H), 5.59 (t, $J$ = 7.0 Hz, 1H), 5.13 (t, $J$ = 6.5 Hz, 1H), 4.94 (d, $J$ = 6.9 Hz, 2H), 2.22−2.17 (m, 4H), 1.78 (s, 3H), 1.70 (s, 3H), 1.63 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) 175.9, 158.4, 142.7, 134.2, 132.7, 131.8, 131.5, 130.6, 129.5, 129.4, 128.5, 128.4, 123.7, 118.2, 64.8, 39.6, 26.3, 25.7, 17.7, 16.7 ppm; IR (film) 1672, 1654, 1600 cm$^{-1}$; MS (CI) $m/z$ 362.2124 (362.2120 calcd for $C_{24}H_{28}NO_2$).

**General Procedure for $PdCl_2$-Catalyzed Rearrangement of Allylic *N*-Benzoylbenzimidates. *N*-(1-Ethenylbutyl)dibenzamide (16)**. A solution of **7** (0.61 g, 2.0 mmol), $PdCl_2(MeCN)_2$ (26 mg, 0.1 mmol), and toluene (4 mL) was maintained at rt for 6 h and then concentrated. Purification of the residue by flash chromatography (20:1 hexane−EtOAc) yielded 0.55 g (90%) of **16** as a colorless oil that was homogeneous by TLC analysis: $R_f$ 0.17 (9:1 hexane−EtOAc); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.37 (d, $J$ = 7.2 Hz, 4H), 7.20 (t, $J$ = 6.6 Hz, 2H), 7.10 (t, $J$ = 7.7 Hz, 4H), 6.32 (ddd, $J$ = 17.2, 10.1, 7.9 Hz, 1H), 5.32 (d, $J$ = 17.2 Hz, 1H), 5.21−5.14 (m, 2H), 2.20−2.10 (m, 1H), 2.00−1.88 (m, 1H), 1.45 (sextet, $J$ = 7.2 Hz, 2H), 0.97 (t, $J$ = 7.3 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) 173.9, 137.5, 137.1, 131.4, 128.4, 128.0, 117.6, 61.2, 34.5, 19.8, 13.6 ppm; IR (film) 1696, 1654, 1599 cm$^{-1}$; MS (CI) $m/z$ 308.1646 (308.1650 calcd for $C_{20}H_{22}NO_2$). Anal. Calcd for $C_{20}H_{21}NO_2$: C, 78.15; H, 6.89; N, 4.56. Found: C, 78.04; H, 6.88; N, 4.50.

***N*-(1-Phenyl-2(*E*)-butenyl)dibenzamide (12)**. A colorless oil that was homogeneous by TLC analysis: $R_f$ 0.18 (9:1 hexane−EtOAc); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.60 (d, $J$ = 7.8 Hz, 2H), 7.38−7.33 (m, 6H), 7.25 (d, $J$ = 7.5, 1H), 7.21 (t, $J$ = 7.5, 2H), 7.11 (t, $J$ = 7.8 Hz, 4H), 6.47 (dd, $J$ = 15.6, 8.7 Hz, 1H), 6.40 (d, $J$ = 8.8 Hz, 1H), 5.91 (dq, $J$ = 15.0, 6.6 Hz, 1H), 1.80 (dd, $J$ = 6.4, 1.2 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) 173.7, 140.1, 137.6, 137.0, 131.1, 128.6, 128.3, 128.2, 128.0, 127.5, 127.3, 63.4, 17.9 ppm; IR (film) 1698, 1658, 1599, 1581 cm$^{-1}$; MS (EI) $m/z$ 355.1567 (355.1572 calcd for $C_{24}H_{21}NO_2$). Anal. Calcd for $C_{24}H_{21}NO_2$: C, 81.10; H, 5.96; N, 3.94. Found: C, 81.12; H, 6.00; N, 4.91.

***N*-(5-Phenyl-2(*E*)-pentenyl)dibenzamide (13)**. A colorless oil that was homogeneous by TLC analysis: $R_f$ 0.17 (9:1 hexane−EtOAc); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.45 (d, $J$ = 7.0 Hz, 4H), 7.31−7.11 (m, 11H), 5.89−5.71 (m, 2H), 4.58 (d, $J$ = 5.2 Hz, 2H), 2.70 (t, $J$ = 7.6 Hz, 2H), 2.43−2.34 (m, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) 173.8, 141.4, 136.4, 134.5, 131.6, 128.6, 128.3, 128.1, 125.6, 124.7, 48.5, 35.3, 33.8 ppm; IR (film) 1694, 1682, 1651, 1600 cm$^{-1}$; MS (CI) $m/z$ 370.1802 (370.1807 calcd for $C_{25}H_{24}NO_2$). Anal. Calcd for $C_{25}H_{23}NO_2$: C, 81.27; H, 6.27; N, 3.79. Found: C, 81.34; H, 6.31; N, 3.72.

***N*-(2-Methyl-2(*E*)-heptenyl)dibenzamide (14)**. A colorless oil that was homogeneous by TLC analysis. Analytical GLC analysis indicated 98.0% *E* ($PdCl_2$-catalyzed rearrangement) and 98.1% *E* (thermal rearrangement): $R_f$ 0.23 (9:1 hexane−EtOAc);

(11) N-Benzoylbenzimidates were too susceptible to hydrolysis to obtain correct elemental analyses routinely.

$^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.48 (d, $J$ = 7.9 Hz, 4H), 7.27 (t, $J$ = 7.4 Hz, 2H), 7.18 (t, $J$ = 6.9 Hz, 4H), 5.43 (t, $J$ = 7.2 Hz, 1H), 4.56 (s, 2H), 2.01 (q, $J$ = 6.8 Hz, 2H), 1.75 (s, 3H), 1.33−1.20 (m, 4H), 0.83 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) 174.1, 136.5, 131.7, 130.0, 129.0, 128.2, 53.9, 31.5, 27.4, 22.2, 14.8, 13.9 ppm; IR (film) 1698, 1655 cm$^{-1}$; MS (CI) $m/z$ 336.1956 (336.1963 calcd for $C_{22}H_{26}NO_2$). Anal. Calcd for $C_{22}H_{25}NO_2$: C, 78.77; H, 7.51; N, 4.18. Found: C, 78.67; H, 7.54; N, 4.12.

***N*-(2-Cyclohexenyl)dibenzamide (15)**. A colorless oil that was homogeneous by TLC analysis: $R_f$ 0.18 (9:1 hexane−EtOAc); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.39 (d, $J$ = 6.9 Hz, 4H), 7.23 (t, $J$ = 7.4 Hz, 2H), 7.13 (t, $J$ = 7.0 Hz, 4H), 5.94−5.86 (m, 1H), 5.73−5.66 (m, 1H), 5.43−5.33 (m, 1H), 2.40−2.26 (m, 1H), 2.26−1.89 (m, 4H), 1.83−1.64 (m, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) 174.0, 137.7, 131.7, 129.5, 128.6, 128.2, 127.6, 55.5, 27.7, 24.3, 22.0 ppm; IR (film) 1698, 1654, 1602 cm$^{-1}$; MS (CI) $m/z$ 306.1501 (306.1494 calcd for $C_{20}H_{20}NO_2$). Anal. Calcd for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.54; H, 6.33; N, 4.51.

***N*-(1-Phenyl-2-propenyl)dibenzamide (17)**. A colorless oil that was homogeneous by TLC analysis: $R_f$ 0.14 (9:1 hexane−EtOAc); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.62 (d, $J$ = 7.5 Hz, 2H), 7.38 (d, $J$ = 7.1 Hz, 5H), 7.26 (t, $J$ = 7.1 Hz, 2H), 7.21 (t, $J$ = 6.2 Hz, 2H), 7.11 (t, $J$ = 7.4 Hz, 4H), 6.78 (ddd, $J$ = 17.1, 9.9, 8.0 Hz, 1H), 6.45 (d, $J$ = 8.0 Hz, 1H), 5.45 (d, $J$ = 17.1 Hz, 1H), 5.41 (d, $J$ = 9.9 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) 173.6, 139.2, 137.4, 135.3, 131.7, 128.6, 128.4, 128.2, 127.6, 127.5, 119.4, 63.7 ppm; IR (film) 1697, 1655, 1599 cm$^{-1}$; MS (EI) $m/z$ 341.1412 (341.1416 calcd for $C_{23}H_{19}NO_2$). Anal. Calcd for $C_{23}H_{19}NO_2$: C, 80.90; H, 5.61; N, 4.10. Found: C, 80.88; H, 5.67; N, 4.10.

***N*-(1,1-Dimethyl-2-propenyl)dibenzamide (18)**. A colorless oil that was homogeneous by TLC analysis: $R_f$ 0.19 (9:1 hexane−EtOAc); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.38 (d, $J$ = 7.2 Hz, 4H), 7.24 (t, $J$ = 7.2 Hz, 2H), 7.12 (t, $J$ = 7.5 Hz, 4H), 6.46 (dd, $J$ = 17.4, 10.7 Hz, 1H), 5.26 (d, $J$ = 17.4 Hz, 1H), 5.14 (d, $J$ = 10.7 Hz, 1H), 1.76 (s, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$) 173.4, 144.3, 138.3, 131.6, 128.7, 128.4, 128.1, 111.6, 62.5, 27.3 ppm; IR (film) 1702, 1658, 1598 cm$^{-1}$; MS (CI) $m/z$ 294.1485 (294.1494 calcd for $C_{19}H_{20}NO_2$). Anal. Calcd for $C_{19}H_{19}NO_2$: C, 77.79; H, 6.53; N, 4.77. Found: C, 77.60; H, 6.47; N, 4.72.

***N*-(1,5-Dimethyl-1-ethenyl-4-hexenyl)dibenzamide (19)**. A colorless oil that was homogeneous by TLC analysis: $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.37 (d, $J$ = 8.2 Hz, 4H), 7.23 (t, $J$ = 8.3 Hz, 2H), 7.13 (t, $J$ = 8.2 Hz, 4H), 6.58 (dd, $J$ = 15.2, 10.4 Hz, 1H), 5.25−5.15 (m, 3H), 2.39−2.32 (m, 1H), 2.23−2.15 (m, 2H), 2.11−2.05 (m, 1H), 1.72 (s, 3H), 1.67 (s, 3H), 1.60 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) 173.8, 158.2, 143.0, 134.1, 133.0, 131.8, 129.6, 128.5, 118.2, 67.0, 40.1, 26.4, 25.8, 17.6, 16.4 ppm; IR (film) 1702, 1667, 1602 cm$^{-1}$; MS (CI) $m/z$ 362.2118 (362.2120 calcd for $C_{24}H_{28}NO_2$).

**Acknowledgment.** This research was supported by National Science Foundation grant CHE-9412266. G.G.Z. was supported in part by a GAANN grant from the Department of Education. NMR and mass spectra were determined using instruments acquired with the assistance of Shared Instrumentation grants from NSF and NIH. We thank Dr. John Greaves for assistance with mass spectral analyses.

**Supporting Information Available:** $^1$H NMR spectra of **3**−**5**, **7**−**11**, and **19** (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO962129Q