3 H, CH_3); GC–MS (70 eV) M^+ 227 (1), 149 (10), 143 (8), 113 (100), 95 (11), 85 (32), 83 (25), 56 (63), 55 (30), 43 (68), 41 (70), 39 (33), 29 (45). Anal. Calcd for $C_8H_{12}O_3Cl_2$: C, 42.29; H, 5.29. Found: C, 41.99; H, 5.36.

5-(2,2-Dichloroethenyl)dihydro-4,4-dimethyl-2(3*H*)-furanone (2). A mixture of **8** (6.81 g, 0.03 g, 0.03 mol), *p*-toluenesulfonyl chloride (8.33 g, 0.035 mol), and 20% aqueous sodium hydroxide solution (18 mL, 0.09 mol) was stirred at 25 °C for 3 h. The reaction mixture was extracted with chloroform (3 × 30 mL), and the organic layer was dried over anhydrous sodium sulfate. Removal of solvent yielded **2** (5.01 g, 80%), which was distilled under vacuum to yield pure **2** as a pale yellow oil: bp 100–101 °C/0.5 mmHg; 97% (GC); IR ($CHCl_3$) (ν, cm^{-1}) 1795 1740 (s), 1630; ^1H NMR (80 MHz) δ 5.94 (d, 1 H, J = 11 Hz, CH=), 4.88 (d, 1 H, J = 11 Hz, CHO), 2.4 (d, 2 H, J = 1 Hz, CH_2), 1.23 (s, 3 H, CH_3), 1.1 (s, 3 H, CH_3).

Reaction of Pyranone 4 with $KMnO_4$ in 30% Aqueous Acetic Acid. Pyranone **4** was prepared from keto acid **5** by acid-catalyzed dehydration in refluxing toluene with simultaneous removal of water azeotropically.[10] The product was distilled to yield pure **4**: bp 38–40 °C/0.6 mmHg; 99% (GC); IR ($CHCl_3$) (ν, cm^{-1}) 1770, 1700; ^1H NMR δ 4.87 (s, 1 H, CH=), 2.40 (s, 2 H, CH_2), 1.86 (d, 3 H, J = 1.3 Hz, CH_3), 1.08 (s, 6 H, 2 CH_3).

To a solution of pyranone **4** (420 mg, 3 mmol) in 30% aqueous acetic acid (4.0 mL) cooled in an ice water bath was added $KMnO_4$ (237 mg, 1.5 mmol). The usual workup provided a neutral fraction (320 mg) containing 65% **4** and 35% **3** (as analyzed by NMR or GC) and an acidic fraction (80 mg) containing keto acid **5** (15%) (by NMR) and 2,2-dimethylsuccinic acid, mp 138–140 °C (lit.[11] mp 141 °C).

Acknowledgment. We thank IEL Limited for support and the Tata Institute of Fundamental Research, Bombay, for 500-MHz NMR facilities.

Registry No. *trans*-(±)-**1a**, 55701-07-0; *cis*-(±)-**1a**, 55701-06-9; **2**, 115118-27-9; **3**, 115118-28-0; **4**, 68208-62-8; **5**, 20624-63-9; **6**, 78-59-1; **7**, 115118-29-1; **8** (diastereomer 1), 115118-30-4; **8** (diastereomer 2), 115118-31-5.

(11) *Dictionary of Organic Compounds*, 5th ed.; Cadogan, J. I. G., Raphael, R. A., Rees, C. W., Eds.; Chapman and Hall: London, 1982; Vol. 2, p 2096.

An Efficient, Palladium-Catalyzed Route to Protected Allylic Amines

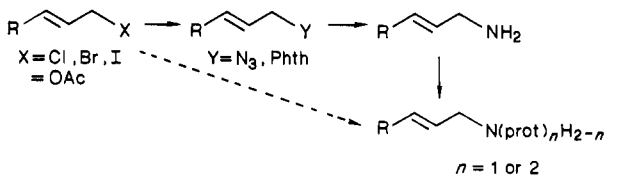
Richard D. Connell,[1] Tobias Rein,[2] Björn Åkermark,*[,2] and Paul Helquist*[,1]

Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556, and Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden

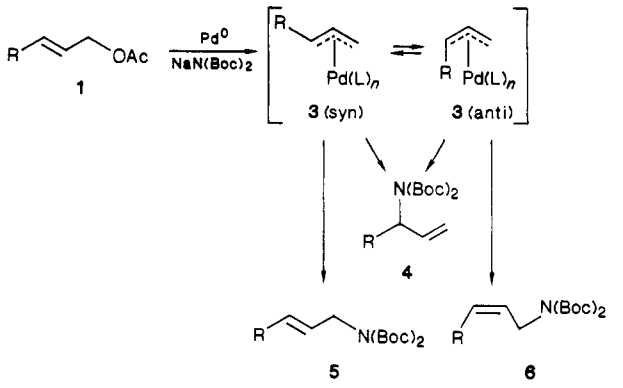
Received January 20, 1988

Because of their occurrence in a number of natural products, the development of methodology directed toward the synthesis of primary allylic amines is an active area of research in organic chemistry.[3,4] Among the methods that have been developed is the palladium-catalyzed conversion of allylic acetates and chlorides to the corresponding amines. Phthalimide,[5] sodium azide,[6] *p*-toluenesulfonamide,[7] and 4,4′-dimethoxybenzhydrylamine[8] have been shown to be useful nucleophiles in these reactions. Although the intermediates formed from these reactions can then be converted to the amine, the conditions for this transformation are often quite harsh. For example, phthalimides are often removed by hydrazine in refluxing ethanol, while the substituted benzhydrylamine group is subjected to hot formic acid to effect cleavage.

Scheme I

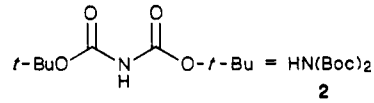


Scheme II



As part of our ongoing interest in the synthesis of various antibiotics, we sought to develop a direct method for the conversion of allylic acetates into suitably protected primary amines. Such an approach would avoid the multistep sequences involved with substitution reactions of azide and phthalimide (Scheme I).

To this end, we began to study acetamide and *t*-butyl carbamate as nucleophiles. Their reactions would supposedly lead directly to N-acyl- and *N*-Boc-protected primary amines.[9] Unfortunately, these compounds were unreactive as nucleophiles in both their neutral and metalated forms.[10] Based on the successful use of malonates and other stabilized nucleophiles in palladium-catalyzed reactions,[11] we then looked at di-*tert*-butyl iminodicarbonate (**2**) as a nucleophile.

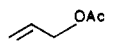
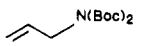
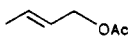
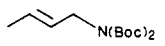
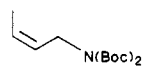
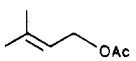
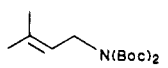
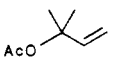
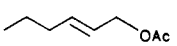
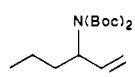
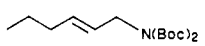
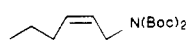
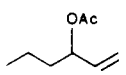
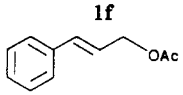
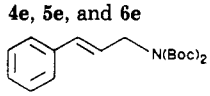
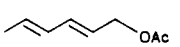
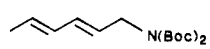
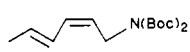
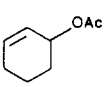
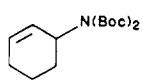


2

(1) University of Notre Dame.
(2) Royal Institute of Technology.
(3) For an excellent review of synthetic approaches to primary allylic amines, see: Cheikh, R. B.; Chaabouni, R.; Laurent, A.; Mison, P.; Nafti, A. *Synthesis* **1983**, 685–700.
(4) For recent developments of methodology in this area, see: (a) Germon, C.; Alexakis, A.; Normant, J. F. *Synthesis* **1984**, 40–43. (b) Inoue, Y.; Taguchi, M.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2721–2722. (c) Corriu, R. J. P.; Huynh, V.; Iqbal, J.; Moreau, J. J. E. *J. Organomet. Chem.* **1984**, *276*, C61–C64. (d) Inaba, M.; Moriwake, T.; Saito, S. *Tetrahedron Lett.* **1985**, *26*, 3235–3238. (e) Betancor, C.; Carrau, R.; Francisco, C. G.; Suārez E. *Tetrahedron Lett.* **1986**, *27*, 4783–4786. (f) Bargar, T. M.; McCowan, J. R.; McCarthy, J. R.; Wagner, E. R. *J. Org. Chem.* **1987**, *52*, 678–681.
(5) Inoue, Y.; Taguchi, M.; Toyofuku, M.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 3021–3022.
(6) Murahashi, S.; Tanigawa, Y.; Imada, Y.; Taniguchi, Y. *Tetrahedron Lett.* **1986**, *27*, 227–230.
(7) Byström, S.; Aslanian, R.; Backväll, J. E. *Tetrahedron Lett.* **1985**, *26*, 1749–1752.
(8) Trost, B. M.; Keinan, E. *J. Org. Chem.* **1979**, *44*, 3451–3457.
(9) 2-Butenylene-1,4-dicarbamates have been found to N-alkylate π-allyls in an intramolecular fashion to provide 4-vinyloxazolidones: Hayashi, T.; Yamamoto, A.; Ito, Y. *Tetrahedron Lett.* **1987**, *28*, 4837–4840.
(10) Recently, Hegedus has also noted some difficulty in employing amides as nucleophiles in palladium-catalyzed reactions: Harrington, P. J.; Hegedus, L. S.; McDaniel, K. F. *J. Am. Chem. Soc.* **1987**, *109*, 4335–4338.
(11) For excellent reviews of this type of reaction as well as useful references, see: (a) Tsuji, J.; Minami, I. *Acc. Chem. Res.* **1987**, *20*, 140–145. (b) Trost, B. M. *Tetrahedron* **1977**, *33*, 2615–2649.

0022-3263/88/1953-3845$01.50/0

Table I. Conversion of Allylic Acetates to Protected Allylic Amines Using Palladium Catalysis

acetate	reaction conditions	yield (%)[a]	products		
 **1a**	lithium salt, 36 h at 25 °C	93[b]	 **4a**		
 **1b**	lithium salt, 36 h at 25 °C	94[b]	 **4b**	 **5b** (42:50:8)[c]	 **6b**
 **1c**	sodium salt, 48 h at 45 °C	44	 **5c**		
 **1d**	lithium salt, 144 h at 45 °C	25	**5c**		
 **1e**	sodium salt, 48 h at 45 °C	81	 **4e**	 **5e** (8:78:14)[c]	 **6e**
 **1f**	sodium salt, 30 h at 45 °C	98	**4e**, **5e**, and **6e**	(12:77:11)[c]	
1f	lithium salt, 72 h at 25 °C	100	**4e**, **5e**, and **6e**	(6:87:7)[c]	
 **1g**	sodium salt, 36 h at 25 °C	85[b]	 **5g**		
 **1h**	lithium salt, 160 h at 25 °C	84	 **5h** (85:15)[c]	 **6h**	
 **1i**	sodium salt, 36 h at 45 °C	57	 **6i**		

[a] Refers to isolated yield after column chromatography. [b] Only 4% catalyst employed; 5% used in all other cases. [c] Ratio determined by ^{1}H NMR integration of the C-1 protons in the mixture prior to chromatography.

Although **2** was developed over 20 years ago by Carpino,[12] its application as an amine equivalent has been limited by what Carpino himself referred to as a lack of an efficient synthesis.[13] Recently, a greatly improved synthesis has been developed by Ragnarsson,[14] and **2** is now readily prepared and is even available commercially.[15] Therefore, we began to explore palladium-catalyzed reactions of **2** with allylic acetates.

When the sodium or potassium salt of **2** was added to a warm DMF solution of 1-acetoxy-2-hexene (**1e**, R = N-propyl), a mixture of isomeric diprotected amines **4–6** was obtained. These products may all be derived from the same π-allyl intermediate which can be attacked at either the C-1 or C-3 position (Scheme II). Prior to the attack of the nucleophile, the π-allyl complex **3** can equilibrate between the syn and anti forms, thus giving rise to three possible products. To determine which factors influence the distribution of these products, we studied a number of allylic acetates and reaction conditions. The results of this study are summarized in Table I.

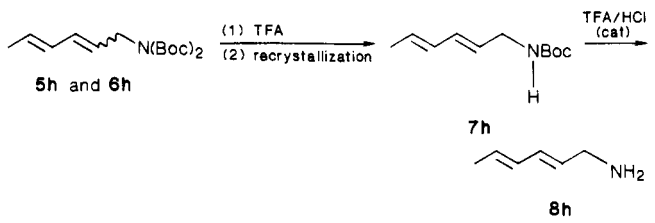
In all cases, the active catalyst was formed in situ by adding $Pd(dba)_2$ to an appropriate amount of diphos or triphenylphosphine.[16] With respect to the catalyst, we found that the reaction worked very well with diphos as a ligand.[17] Triphenylphosphine worked equally well when used with cinammyl acetate (**1g**) but was ineffective with the conjugated acetate **1h** and the other acetates. Thus all entries in Table I employed diphos as the ligand.

From the results in Table I, it appears that the rate and regioselectively of the attack of the nucleophile is very sensitive to the substitution pattern around the π-allyl complex. When the allylic acetate is unsubstituted (**1a**), the reaction is relatively fast, and high yields of the desired product are obtained. If the acetate (and thus the π-allyl) is substituted, high chemical yields are still obtained, but the reaction proceeds more slowly, and mixtures of isomers are obtained.[18] When the acetate is geminally disubstituted (**1c** and **1d**), the selectivity of attack at the less substituted end of the π-allyl is enhanced, and only **5c** is obtained, albeit in low yields.

In the hopes of improving the isomer ratio, we attempted the same reactions as above but at lower temperatures. We

(12) (a) Carpino, L. A. *J. Org. Chem.* **1964**, *29*, 2820–2824. (b) Felix, A. M.; Fryer, R. I. *J. Heterocycl. Chem.* **1968**, *5*, 291–293. (c) Allan, R. D.; Johnston, G. A.; Kazlauskas, R.; Tran, H. W. *J. Chem. Soc., Perkin Trans. 1*, **1983**, 2983–2985.
(13) Carpino, L. A. *Acc. Chem. Res.* **1973**, *6*, 191–198.
(14) Grehn, L.; Ragnarsson, U. *Synthesis* **1987**, 275–276.
(15) Fluka Chemical Corp.
(16) For the preparation of bis(benzilideneacetone)palladium(0), see: Rettig, M. F.; Maitlis, P. M. *Inorg. Synth.* **1977**, *17*, 135.
(17) The 1,2-bis(diphenylphosphino)ethane (diphos) was recrystallized prior to use. We found that recrystallization from heptane was very important to the speed and the yield of the reaction.
(18) With cinnamyl acetate (**1g**), the lithium, sodium, and potassium salts of **2** all provide the pure trans product **5g** in uniformly high yields.

Scheme III



found, however, that the sodium and potassium salts of **2** were not very soluble in THF or mixtures of THF and DMF at room temperature. When only DMF was used as a solvent, the reaction was faster, but still nonselective. We then explored the lithium salt of **2** and found this salt to be more soluble in THF/DMF mixtures at 25 °C. This solubility, along with the lower temperatures that could be used, led to higher yields and improved selectivity. For example, the reaction of **1f** with the lithium salt of **2**, performed at 25 °C, provided the same high yield of product as the sodium salt but with improved selectivity. Another example of the importance of the counterion on reactivity are the results with acetates **1c**, **1d**, and **1i**. Here we found that the sodium salt was the counterion of choice. The same reactions with the lithium salt of **2** with these hindered acetates led to much lower yields of the desired product. Because the starting material was completely consumed in these three examples, the low yields may reflect an elimination reaction of the sterically hindered π-allyl complexes to give 1,3-dienes. Such elimination reactions of π-allyls generated from allylic acetates have been shown to occur at room temperature under basic conditions.[19]

With the desired diprotected amines in hand, we then looked ahead toward deprotection to give the primary amines. While concentrated HCl[12a] and HBr/HOAc[12c] have been used to remove both carboxylate groups, we found that treatment of the iminodicarbonate with trifluoroacetic acid at room temperature provided high yields of the carbamate. Although this kind of partial deprotection has been reported under basic conditions for unsymmetrical iminodicarbonates,[20] the present result indicates the usefulness of an acidic partial hydrolysis of a *tert*-butyl iminodicarbonate. This selective deprotection turned out to be of general scope and was extended to other substrates (**4e**, **5e**, **5g** in Experimental Section).

The fact that some of the monoprotected amines were crystalline proved to be advantageous. For example, when the isomeric mixture of **5h** and **6h** was treated with 1.5 equiv of trifluoroacetic acid at room temperature, the corresponding mixture of isomeric carbamates was obtained as a waxy oil. However, recrystallization of this mixture from hexane provided the 2*E*,4*E* isomer in isomerically pure form (Scheme III). The unprotected amine was then obtained by a second acid-catalyzed hydrolysis under mild conditions.

In summary, we have developed a mild and high yielding route to protected allylic amines from allylic acetates. These substrates can be selectively deprotected to the corresponding monoprotected amines or can be converted directly to allylic amines by using previously described methods. Because of the gentle conditions required for substitution as well as the mildness of deprotection, this transformation is well suited for applications to complex syntheses.

(19) (a) Coste-Manière. I. C.; Zahra, J. P.; Waegell, B. *Tetrahedron Lett.* **1988**, *29*, 1017–1020. (b) Trost, B. M.; Tometzki, G. B. *J. Org. Chem.* **1988**, *53*, 915–917. (c) Trost, B. M.; Mignani, S. *J. Org. Chem.* **1986**, *51*, 3435–3439. (d) Åkermark, B.; Nyström, J. E.; Rein, T.; Bäckvall, J. E.; Helquist, P.; Aslanian, R. *Tetrahedron Lett.* **1984**, *25*, 5719–5722, and references cited in these articles.

(20) (a) Clarke, C. T.; Elliott, J. D.; Jones, J. H. *J. Chem. Soc., Perkin Trans. 1*, **1978**, 1088–1090. (b) Elliott, J. D.; Jones, J. H. *J. Chem. Soc., Chem. Commun.* **1977**, 758–759.

Experimental Section

All reactions were carried out in oven-dried glassware (120 °C) which was cooled under nitrogen. Anhydrous tetrahydrofuran (THF) was freshly distilled under nitrogen from deep purple or dark blue solutions of sodium benzophenone radical anion or dianion. Dimethyl formamide was dried over activated 4A molecular sieves. Crude products were purified by flash column chromatography using 250-mesh silica gel. Thin layer chromatography (TLC) was performed on aluminum-backed silica gel plates, and visualization was accomplished with a UV light or an iodine vapor chamber.

Proton (^{1}H) nuclear magnetic resonance (NMR) spectra were obtained on a Magnachem A-200 (200 MHz) or a Nicolet NT-300 (300 MHz) spectrometer. Carbon (^{13}C) NMR were obtained on these same spectrometers at 50 or 75 MHz, respectively. Tetramethylsilane (TMS) and deuteriated chloroform ($CDCl_3$) were used as internal standards. Chemical shifts are reported in parts per million (δ) downfield from TMS, and proton NMR peak integrations are reported as the relative number of hydrogen atoms (H). The infrared (IR) spectra were obtained on a Perkin-Elmer Model 1420 ratio recording spectrophotometer as neat liquids or as solutions and were calibrated by using a polystyrene standard (1601 cm^{-1}). Mass spectral data were obtained on a Finnigan MAT Model 8430 spectrometer using electron impact ionization (EI) at 70 eV. Elemental analyses were performed by M-H-W Laboratories (Phoenix, AZ). Melting points were obtained on a Thomas Hoover capillary melting point apparatus in open-ended capillaries and are corrected.

General Procedure for the Conversion of Allylic Acetates to Allylic Amines Using Sodium Hydride as a Base. 3-[Bis(*tert*-butoxycarbonyl)amino]-1-phenyl-1-propene (5g). Into a 50-mL conical flask equipped with a magnetic stirrer was added di-*tert*-butyl iminodicarbonate (0.955 g, 4.40 mmol, 1.10 equiv), sodium hydride (0.109 g, 4.40 mmol, 1.10 equiv), DMF (10 mL), and THF (20 mL). The flask was fitted with a condenser, and the solution was warmed to 45 °C under a nitrogen atmosphere for 1 h.

Into a 100-mL round-bottom flask equipped with a magnetic stirrer was added $Pd(dba)_2$ (0.091 g, 0.16 mmol, 4 mol %),[17] diphos (0.089 g, 0.22 mmol),[16] and then cinnamyl acetate (**1g**, 0.705 g, 4.0 mmol, 1.0 equiv). The flask was fitted with a condenser and purged with nitrogen. THF (20 mL) was added, and the solution was again purged with nitrogen. The solution was warmed to 45 °C and stirred at this temperature for 5 min.

To this 100-mL round-bottom flask was added the slurry of sodium di-*tert*-butyl iminodicarbonate along with 10 mL of fresh DMF via cannula. When the addition was complete, the cannula was removed and the reaction vessel was again purged with nitrogen. The reaction mixture was maintained at 45 °C and monitored by GC and TLC.

After 12 h at 45 °C, the reaction mixture was cooled to 23 °C and poured into ether (100 mL). The ether phase was washed with water (2 × 10 mL), saturated aqueous $NaHSO_3$ (1 × 10 mL), and saturated aqueous NaCl (1 × 10 mL). The yellow solution was dried ($MgSO_4$) and concentrated in vacuo to provide a yellow oil which was purified by flash chromatography (5.0% ethyl acetate in hexane) to provide 1.136 g (85%) of **5g** as a pale yellow oil: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.27 (m, 5 H, Ar H), 6.44 (d, $J_{2,3}$ = 16.1 Hz, PhC*H*=CHCH$_2$N), 6.12 (dt, $J_{2,3}$ = 16.1 Hz, $J_{1,2}$ = 6.3 Hz, PhCH=C*H*CH$_2$N), 4.23 (dd, $J_{1,2}$ = 6.3 Hz, $J_{1,3}$ = 1.0 Hz, PhCH=CHC*H*$_2$N), 1.49 (s, 18 H, COOC(C*H*$_3$)$_3$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 152.19 (*C*OOC(CH$_3$)$_3$), 136.65, 132.16, 128.39, 127.44, 126.23 and 124.96 (*C*$_6$H$_5$CH=*C*H), 82.19 (*C*H$_2$N), 48.01 (COO*C*(CH$_3$)$_3$), 27.95 (COOC(*C*H$_3$)$_3$); IR (neat) 1750, 1690 cm^{-1}; mass spectrum (CI), *m*/*z* (rel intensity) 334 (10, M + H), 278 (96, M + 1 − C$_4$H$_8$), 222 (100, M + 1 − 2C$_4$H$_8$), 178 (30, M + 1 − 2C$_4$H$_8$ − CO$_2$). Anal. Calcd for $C_{19}H_{27}NO_4$: C, 68.44; H, 8.16. Found: C, 68.31; H, 8.19.

General Procedure for the Conversion of Allylic Acetates to Allylic Amines Using *n*-Butyllithium as a Base. Reaction

with 3-Acetoxy-1-hexene (1f). Into a 100-mL round-bottom flask equipped with a magnetic stirrer was added di-*tert*-butyl iminodicarbonate (0.499 g, 2.30 mmol, 1.15 equiv). The flask was fitted with a septum and THF (30 mL) was added. The solution was stirred at 25 °C until the iminodicarbonate was dissolved, and then the flask was placed in a 0 °C ice bath. After 15 min at 0 °C, a solution of *n*-butyllithium (1.32 mL of a 1.6 M solution, 2.10 mmol, 1.10 equiv) was added, and the solution was stirred at 0 °C. After 30 min at 0 °C, the flask was removed from the ice bath, and the solution was stirred at 25 °C for 1 h. To this newly formed white slurry were added 3-acetoxy-1-hexene (**1f**, 0.284 g, 2.0 mmol, 1.0 equiv), $Pd(dba)_2$ (0.057 g, 0.10 mmol), diphos (0.059 g, 0.15 mmol), and THF (20 mL). The flask was purged with nitrogen and stirred at 25 °C.

After 72 h, the reaction mixture was poured into ether (100 mL) and washed with water (2 × 10 mL), saturated aqueous $NaHSO_3$ (1 × 10 mL), and saturated aqueous NaCl (1 × 10 mL). The yellow solution was dried ($MgSO_4$) and concentrated in vacuo to give a yellow oil which was purified by flash chromatography (2.5% ethyl acetate in hexane) to provide 0.597 g (100%) of **4e**, **5e**, and **6e** as a 6:87:7 mixture of isomers. It was possible to obtain fractions containing pure **4e** (first fractions off column) and pure **5e** (last fractions off column). It was not possible to obtain the cis isomer **6e** in isomerically pure form (middle fractions). Its presence was indicated by a doublet at 4.1 ppm and could only be obtained as a mixture along with **4e** and **5e**.

3-[Bis(*tert*-butoxycarbonyl)amino]-1-hexene (4e) was obtained as a colorless oil: ^1H NMR (200 MHz, $CDCl_3$) δ 5.99 (ddd, $J_{1Z,2}$ = 17.2 Hz, $J_{1E,2}$ = 10.2 Hz, $J_{2,3}$ = 6.7 Hz, C*H*=$(H_E)H_Z$), 5.16 (ddd, $J_{1Z,2}$ = 17.2 Hz, $J_{1Z,1E}$ = 1.5 Hz, $J_{1Z,3}$ = 1.4 Hz, CH=C-$(H_E)H_Z$), 5.09 (ddd, $J_{1E,2}$ = 10.2 Hz, $J_{1E,1Z}$ = 1.5 Hz, $J_{1E,3}$ = 1.4 Hz, CH=C$(H_E)H_Z$), 4.63 (tdt, $J_{3,4}$ = 8.3 Hz, $J_{2,3}$ = 6.8 Hz, $J_{1,3}$ = 1.4 Hz, $CH_2CH(N)CH{=}CH_2$), 1.76 (m, 2 H, CH_2CH_2CHN), 1.49 (s, 18 H, $COOC(CH_3)_3$), 1.32 (m, 2 H, CH_3CH_2CHN), 0.92 (t, $J_{5,6}$ = 7.3 Hz, CH_3CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ 153.01 (*COO*-$C(CH_3)_3$), 137.92 (*CH*=CH_2), 115.99 (CH=*CH*$_2$), 81.93 (*CH*-(N)CH=CH_2), 58.91 ($COOC(CH_3)_3$), 34.59 (CH_2CHN), 27.97 ($COOC(CH_3)_3$), 19.52 (CH_3CH_2), 13.74 (CH_3CH_2); IR (neat) 1750, 1710 cm^{-1}; mass spectrum (CI), *m/z* (rel intensity) 300 (15, M + H), 244 (100, M + 1 - C_4H_8), 188 (100, M + 1 - $2C_4H_8$), 144 (22, M + 1 - $2C_4H_8$ - CO_2), 100 (20, M + 1 - $2C_4H_8$ - $2CO_2$).

Anal. Calcd for $C_{16}H_{29}NO_4$: C, 64.18; H, 9.76. Found: C, 64.30; H, 9.73.

1-[Bis(*tert*-butoxycarbonyl)amino]-2(*E*)-hexene (5e) was obtained as a colorless oil: ^1H NMR (200 MHz, $CDCl_3$) δ 5.45 (dm, $J_{2,3}$ = 16.1 Hz, C*H*=C*H*CH_2N), 4.01 (dd, $J_{1,2}$ = 5.6 Hz, $J_{1,3}$ = 1.0 Hz, CH=CHCH_2N), 1.92 (m, 2 H, $CH_2CH_2CH{=}C$), 1.50 (s, 18 H, $COOC(CH_3)_3$), 1.32 (m, 2 H, $CH_3CH_2CH_2$), 0.89 (t, $J_{5,6}$ = 7.3 Hz, CH_3CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ 152.28 (*COO*-$C(CH_3)_3$), 133.44 and 125.20 (*CH*=*CH*CH_2N), 81.89 (CH_2N), 47.90 ($COOC(CH_3)_3$), 34.21 ($CH_2CH{=}C$), 27.96 ($COOC(CH_3)_3$), 22.23 (CH_3CH_2), 13.50 (CH_3CH_2); IR (neat) 1750, 1710 cm^{-1}; mass spectrum (CI), *m/z* (rel intensity) 300 (18, M + 1), 244 (100, M + 1 -C_4H_8), 188 (88, M + 1 - $2C_4H_8$), 144 (22, M + 1 - $2C_4H_8$ - CO_2).

Anal. Calcd for $C_{16}H_{29}NO_4$: C, 64.18; H, 9.76. Found: C, 64.10; H, 9.86.

1-[Bis(*tert*-butoxycarbonyl)amino]-2-propene (4a) was prepared from **1a** (0.500 g, 5.0 mmol) to provide 1.19 g (93%) of **4a** as a white solid: mp 47–48 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 5.83 (ddd, $J_{3Z,2}$ = 17.1 Hz, $J_{3E,2}$ = 10.4 Hz, $J_{1,2}$ = 5.3 Hz, 1 H, $NCH_2CH{=}C(H_E)H_Z$), 5.15 (ddd, $J_{3Z,2}$ = 17.0 Hz, $J_{1,3Z}$ = 1.5 Hz, $J_{3Z,3E}$ = 1.4 Hz, $NCH_2CH{=}C(H_E)H_Z$), 5.09 (ddd, $J_{3E,2}$ = 10.5 Hz, $J_{3Z,3E}$ = 1.4 Hz, $J_{1,3E}$ = 1.2 Hz, $NCH_2CH{=}C(H_E)H_Z$), 4.16 (ddd, $J_{1,2}$ = 5.3 Hz, $J_{1,3Z}$ = 1.5 Hz, $J_{1,3E}$ = 1.2 Hz, $NCH_2CH{=}C(H_E)H_Z$), 1.50 (s, 18 H, $COOC(CH_3)_3$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 151.81 ($COOC(CH_3)_3$), 133.36 ($NCH_2CH{=}CH_2$), 115.69 ($NCH_2CH{=}C$-H_2), 81.65 ($NCH_2CH{=}CH_2$), 48.00 ($COOC(CH_3)_3$), 27.58 (COO-$C(CH_3)_3$); IR (neat) 1740, 1710 cm^{-1}; mass spectrum (CI), *m/z* (rel intensity) 258 (100, M + 1), 202 (22, M + 1 - C_4H_8), 146 (10, M + 1 - 2 C_4H_8).

Anal. Calcd for $C_{13}H_{23}NO_4$: C, 60.67; H, 9.01. Found: C, 60.54; H, 9.05.

Reaction with Crotyl Acetate (1b). Performed with **1b** (0.570 g, 5.0 mmol) to provide 1.27 g (94%) of **4b**, **5b**, and **6b** as a 42:50:6 mixture of isomers. It was possible to obtain fractions containing pure **4b** (first fractions off column) and pure **5b** (last fractions off column). It was not possible to obtain the cis isomer **6b** in isomerically pure form (middle fractions). Its presence was indicated by a doublet at 4.2 ppm (CH_2N) in a mixture with **4b** and **5b**.

3-[Bis(*tert*-butoxycarbonyl)amino]-1-butene (4b) was obtained as a colorless oil: ^1H NMR (200 MHz, $CDCl_3$) δ 6.00 (ddd, $J_{1Z,2}$ = 17.35 Hz, $J_{1E,2}$ = 10.4 Hz, $J_{2,3}$ = 5.6 Hz, 1 H, $CH_3CH(N)CH{=}C(H_E)H_Z$), 5.13 (ddd, $J_{1Z,2}$ = 15.9 Hz, $J_{1Z,3}$ = 1.5 Hz, $J_{1E,1Z}$ = 1.4 Hz, CH(N)CH=$C(H_E)H_Z$), 5.09 (ddd, $J_{1E,2}$ = 10.5 Hz, $J_{1E,3}$ = 1.7 Hz, $J_{1Z,1E}$ = 1.4 Hz, CH(N)CH=$C(H_E)H_Z$), 4.80 (m, $J_{2,3}$ = 7.1 Hz, $J_{1E,3}$ = 1.7 Hz, $CH_3CH(N)CH{=}CH_2$), 1.50 (s, 18 H, $COOC(CH_3)_3$), 1.40 (d, $J_{3,4}$ = 7.1 Hz, $CH_3CH(N)CH{=}CH_2$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 152.00 ($COOC(CH_3)_3$), 138.91 ($CH_3CH(N)CH{=}CH_2$), 114.80 ($CH_3CH(N)CH{=}CH_2$), 81.98 ($CH_3CH(N)CH{=}CH_2$), 53.99 ($COOC(CH_3)_3$), 27.97 ($COOC(C$-$H_3)_3$), 17.88 ($CH_3CH(N)CH{=}C$); IR (neat) 1740, 1710 cm^{-1}; mass spectrum (CI), *m/z* 216 (100, M + 1 - C_4H_8), 160 (58, M + 1 - $2C_4H_8$).

Anal. Calcd for $C_{14}H_{25}NO_4$: C, 61.97; H, 9.29. Found: C, 61.96; H, 9.28.

1-[Bis(*tert*-butoxycarbonyl)amino]-2(*E*)-butene (5b) was obtained as a colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 5.59 (dqt, $J_{2,3}$ = 15.29 Hz, $J_{3,4}$ = 6.22 Hz, $J_{1,3}$ = 0.91 Hz, 1 H, $CH_3CH{=}CHCH_2N$), 5.44 (dtq, $J_{2,3}$ = 15.25 Hz, $J_{1,2}$ = 5.93 Hz, $J_{2,4}$ = 1.30 Hz, 1 H, $CH_3CH{=}CHCH_2N$), 4.08 (dd, $J_{1,2}$ = 5.98 Hz, $J_{1,3}$ = 0.99 Hz, 2 H, $CH_3CH{=}CHCH_2N$), 1.63 (dd, $J_{3,4}$ = 6.21 Hz, $J_{2,4}$ = 1.21 Hz, 3 H, $CH_3CH{=}CHCH_2N$), 1.50 (s, 18 H, $COOC(CH_3)_3$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 152.01 ($COOC(CH_3)_3$), 127.83 and 126.15 (CH=$CHCH_2$), 81.51 ($CH_3CH{=}CHCH_2N$), 47.53 ($COOC(CH_3)_3$), 27.68 ($COOC(CH_3)_3$), 17.23 ($CH_3CH{=}CH$-CH_2N); IR (neat) 1740, 1710 cm^{-1}; mass spectrum (CI), *m/z* (rel intensity) 272 (100, M + 1), 216 (80, M + 1 - C_4H_8), 160 (30, M + 1 - $2C_4H_8$).

Anal. Calcd for $C_{14}H_{25}NO_4$: C, 61.97; H, 9.29. Found: C, 62.10; H, 9.18.

1-[Bis(*tert*-butoxycarbonyl)amino]-3-methyl-2-butene (5c) was prepared from **1c** (0.512 g, 4.0 mmol) to provide 0.501 g (44%) of **5c** as a colorless oil: ^1H NMR (200 MHz, $CDCl_3$) δ 5.18 (tm, $J_{1,2}$ = 6.8 Hz, $J_{2,4}$ = 1.5 Hz, 1 H, C=C*H*CH_2N), 4.15 (d, $J_{1,2}$ = 6.6 Hz, 2 H, $CH_3(CH_3)C{=}CHCH_2N$), 1.73 (s, 3 H, $CH_3(CH_3)$-C=C), 1.69 (s, 3 H, $CH_3(CH_3)C{=}C$), 1.49 (s, 18 H, $COOC(CH_3)_3$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 152.63 ($COOC(CH_3)_3$), 134.62 and 120.81 ($CH_3(CH_3)C{=}CHCH_2N$), 82.00 ($CH_3(CH_3)C{=}CHCH_2N$), 44.35 ($COOC(CH_3)_3$), 28.09 ($COOC(CH_3)_3$), 25.64 ($CH_3(CH_3)C{=}$ $CHCH_2N$), 18.02 ($CH_3(CH_3)C{=}CH$); IR (neat) 1740, 1710 cm^{-1}; mass spectrum (CI); *m/z* (rel intensity) 286 (100, M + 1), 230 (68, M + 1 - C_4H_8), 174 (M + 1 - $2C_4H_8$).

Anal. Calcd for $C_{15}H_{27}NO_4$: C, 63.13; H, 9.53. Found: C, 62.92; H, 9.54.

1-[Bis(*tert*-butoxycarbonyl)amino]-2,4-hexadienes (5h and 6h) were prepared from **1h** (0.980 g, 7.0 mmol) to provide 1.74 g (84%) of **5h** and **6h** as a colorless oil in an 85:15 ratio of isomers: ^1H NMR (200 MHz, $CDCl_3$) δ 6.48 (m, $CH_3CH{=}CH$, **6h**) and 6.15 (m, 2 H, $CH_3CH{=}CHCH{=}CHCH_2N$, **5h** and **6h**), 6.05 (m, 2 H, $CH_3CH{=}CHCH{=}CHCH_2N$, **5h** and **6h**), 4.20 (m, CH=CHC-H_2N, **6h**) and 4.15 (m, CH=$CHCH_2N$, **5h**), 1.77 (d, $J_{5,6}$ = 6.5 Hz, 3 H, CH_3), 1.49 (s, 18 H, $COOC(CH_3)_3$); ^{13}C NMR (50 MHz, $CDCl_3$, **5h** only) δ 152.12 ($NCOOC(CH_3)_3$), 132.69, 130.63, 129.22, and 125.43 ($CH_3CH{=}CHCH{=}CHCH_2$, 81.93 (CH_2N), 47.67 ($COOC$-$(CH_3)_3$), 27.86 ($COOC(CH_3)_3$), 17.85 ($CHCH_3$); IR (neat) 1740, 1710 cm^{-1}; mass spectrum (CI), *m/z* (rel intensity) 298 (100, M + 1), 242 (50, M + 1 - C_4H_8), 186 (44, M + 1 - $2C_4H_8$).

Anal. Calcd for $C_{16}H_{27}NO_4$: C, 64.62; H, 9.15. Found: C, 64.49; H, 9.28.

2-[Bis(*tert*-butoxycarbonyl)amino]cyclohexene (6i) was prepared from **1i** (0.560 g, 4.0 mmol) to provide 0.667 g (57%) of **6i** as a colorless oil: ^1H NMR (200 MHz, $CDCl_3$) δ 5.70 (m, 1 H) and 5.52 (m, 1 H, C*H*=C*H*CHN), 4.76 (m, 1 H, CH=CHC*H*N), 1.94 (m, 4 H) and 1.65 (m, 2 H, $CH_2CH_2CH_2$), 1.49 (s, 18 H, $COOC(CH_3)_3$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 152.68 (*CO*-$OC(CH_3)_3$), 128.80 and 127.53 (*CH*=*CH*CHN), 81.77 (CH=CH-*C*HN), 53.98 ($COOC(CH_3)_3$), 27.79 ($COOC(CH_3)_3$), 27.28, 24.13, and 21.95 ($CH_2CH_2CH_2$); IR (neat) 1750, 1710 cm^{-1}; mass spectrum (CI), *m/z* (rel intensity) 298 (20, M + H), 242 (80, M + 1 - C_4H_8), 186 (100, M + 1 - $2C_4H_8$), 142 (30, M + 1 - $2C_4H_8$ - CO_2).

Anal. Calcd for $C_{16}H_{27}NO_4$: C, 64.62; H, 9.15. Found: C, 64.72; H, 9.21.

General Procedure for Selective Removal of One *tert*-Butoxycarbonyl Group. 1-[(*tert*-Butoxycarbonyl)amino]-2(*E*),4(*E*)-hexadiene (7h). Into a 25-mL round-bottom flask equipped with a magnetic stirrer were added the isomeric mixture of **5h** and **6h** (0.560 g, 1.88 mmol), methylene chloride (20 mL), and trifluoroacetic acid (0.322 g, 2.82 mmol, 1.5 equiv). The flask was fitted with a septum, and the solution was stirred at 25 °C for 20 h. The solution was then poured into ether (70 mL) and washed with 10% aqueous NaOH (1 × 10 mL) and saturated aqueous NaCl (1 × 10 mL). The colorless solution was dried ($MgSO_4$) and concentrated in vacuo to provide 0.362 g (98%) of the monoprotected amine as a mixture of isomers. When this oil was dissolved in a minimal amount of hexane, transferred to a Craig tube, and cooled to −20 °C, a white solid crystallized out of solution. Filtration and a second recrystallization provided **7h** as a white solid (in 60–80% yield): mp 51–53 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.11 (ddt, $J_{2,3}$ = 14.4 Hz, $J_{3,4}$ = 10.4 Hz, $J_{1,3}$ = 1.2 Hz, 1 H, C*H*=CHCH$_2$N), 6.00 (ddq, $J_{4,5}$ = 14.0 Hz, $J_{3,4}$ = 10.3 Hz, $J_{4,6}$ = 1.5 Hz, 1 H, CH$_3$CH=C*H*CH), 5.67 (dq, $J_{4,5}$ = 14.0 Hz, $J_{5,6}$ = 6.57 Hz, 1 H, CH$_3$C*H*=CH), 5.54 (dt, $J_{2,3}$ = 14.5 Hz, $J_{1,2}$ = 6.0 Hz, 1 H, CH=C*H*CH$_2$N), 4.65 (bs, 1 H, N*H*COO(CH$_3$)$_3$), 3.66 (bt, $J_{1,2}$ = 5.4 Hz, CH=CHC*H*$_2$N), 1.77 (d, J = 6.5 Hz, 3 H, CH$_3$CH=CH), 1.44 (s, 9 H, NHCOOC(C*H*$_3$)$_3$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 155.65 (N*C*OOC(CH$_3$)$_3$), 131.88, 130.62, 129.39, and 126.84 (CH$_3$*C*H=*C*H*C*H=*C*H), 79.21 (*C*H$_2$N), 42.35 (COO*C*(CH$_3$)$_3$), 28.33 (COOC(*C*H$_3$)$_3$), 17.96 (*C*HCH$_3$); IR ($CDCl_3$) 3420, 1690 cm^{-1}; mass spectrum (CI), *m/z* (rel intensity) 197 (2, M$^+$), 141 (38, M$^+$ − C$_4$H$_8$), 96 (M$^+$ −C$_4$H$_8$ − CO$_2$), 80 (100).

Anal. Calcd for $C_{11}H_{19}NO_2$: C, 66.97; H, 9.71. Found: C, 67.18; H, 9.73.

3-[(*tert*-Butoxycarbonyl)amino]-1-hexene (7e). Following the same procedure as above, **4e** (0.237 g, 0.79 mmol) in methylene chloride (10 mL) was treated with trifluoroacetic acid (0.135 g, 1.19 mmol, 1.5 equiv) and stirred at 25 °,C for 20 h to provide 0.142 g (90%) of **7e** as a colorless oil: ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.73 (ddd, $J_{1Z,2}$ = 17 Hz, $J_{1E,2}$ = 10.2 Hz, $J_{2,3}$ = 5.8 Hz, 1 H, CHC*H*=C(H$_E$)H$_Z$), 5.13 (ddd, $J_{1Z,2}$ = 17.3 Hz, $J_{1Z,1E}$ = 1.4 Hz, $J_{1Z,3}$ = 1.3 Hz, 1 H, CHCH=C(H$_E$)*H*$_Z$), 5.06 (ddd, $J_{1E,2}$ = 10.2 Hz, $J_{1Z,1E}$ = 1.4 Hz, $J_{1Z,3}$ = 1.2 Hz, 1 H, CHCH=C(*H*$_E$)H$_Z$), 4.52 (bs, N*H*COOC(CH$_3$)$_3$), 4.09 (bt, 1 H, C*H*NHCOOC(CH$_3$)$_3$), 2.10 (m, 2 H, C*H*$_2$CH$_2$CH$_3$), 1.45 (s, 9 H, NHCOOC(C*H*$_3$)$_3$), 1.30 (m, 2 H, CH$_2$C*H*$_2$CH$_3$), 0.92 (t, $J_{5,6}$ = 6.7 Hz, 3 H, CH$_2$CH$_2$C*H*$_3$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 155.33 (*C*OOC(CH$_3$)$_3$), 139.14 (CH$_2$C-H(N)*C*H=CH$_2$), 114.06 (CH$_2$CH(N)C*H*=*C*H$_2$), 79.10 (CH$_2$CH-(N)CH=*C*H$_2$), 52.60 (COO*C*(CH$_3$)$_3$), 37.28 (CH$_3$CH$_2$CH$_2$CHN), 28.33 (COOC(*C*H$_3$)$_3$), 18.85 (CH$_3$*C*H$_2$CH$_2$CHN), 13.78 (*C*H$_3$C-H$_2$CH$_2$CHN); IR (neat) 3350, 1710 cm^{-1}; mass spectrum (CI), *m/z* (rel intensity) 199 (2, M$^+$), 156 (42, M + 1 − CO$_2$), 143 (38, M − C$_4$H$_8$), 100 (100, M + 1 − C$_4$H$_8$ − CO$_2$).

Anal. Calcd for $C_{11}H_{21}NO_2$: C, 66.29; H, 10.62. Found: C, 66.20; H, 10.84.

1-[(*tert*-Butoxycarbonyl)amino]-2(*E*)-hexene (7f). Following the same procedure as above, **5e** (0.626 g, 2.09 mmol), methylene chloride (15 mL), and trifluoroacetic acid (0.358 g, 3.14 mmol, 1.5 equiv) were stirred at 25 °C for 22 h. Workup as above provided 0.389 g (94%) of **7f** as a colorless oil: ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.49 (dm, $J_{2,3}$ = 15.6 Hz, 2 H, CH$_2$C*H*=C*H*CH$_2$N), 4.90 (bs, 1 H, N*H*), 3.66 (bt, $J_{1,2}$ = 5.4 Hz, CH=CHC*H*$_2$NH), 1.98 (m, 2 H, CH$_2$C*H*$_2$CH=CH), 1.44 (s, 9 H, COOC(C*H*$_3$)$_3$), 1.32 (m, 2 H, CH$_3$C*H*$_2$CH$_2$), 0.89 (t, $J_{5,6}$ = 7.3 Hz, C*H*$_3$CH$_2$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 155.53 (*C*OOC(CH$_3$)$_3$), 132.31 and 126.40 (*C*H=*C*H), 78.69 (CH=CH$_2$CH$_2$N), 42.32 (COO*C*(CH$_3$)$_3$), 34.00 (C-H$_3$CH$_2$CH$_2$), 28.13 (COOC(*C*H$_3$)$_3$), 22.02 (CH$_3$CH$_2$CH$_2$), 13.32 (*C*H$_3$CH$_2$CH$_2$); IR (neat) 3360, 1710 cm^{-1}; mass spectrum (CI), *m/z* (rel intensity) 199 (2, M$^+$), 143 (82, M$^+$ − C$_4$H$_8$), 100 (100, M + 1 − C$_4$H$_8$ − CO$_2$).

Anal. Calcd for $C_{11}H_{21}NO_2$: C, 66.29; H, 10.62. Found: C, 66.44; H, 10.68.

3-[(*tert*-Butoxycarbonyl)amino]-1-phenyl-1-propene (7g). Following the same procedure as above, **5g** (0.670 g, 2.01 mmol), methylene chloride (12 mL), and trifluoroacetic acid (0.329 g, 2.88 mmol) were stirred at 25 °C for 19 h. Workup as above provided 0.453 g (97%) of **7g** as a white solid: mp 83–85 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.30 (m, 5 H, Ar H), 6.48 (dt, $J_{2,3}$ = 15.8 Hz, $J_{1,3}$ = 1.5 Hz, PhC*H*=CHCH$_2$N), 6.16 (dt, $J_{2,3}$ = 15.9 Hz, $J_{1,2}$ = 6.1 Hz, PhCH=C*H*CH$_2$N), 4.71 (bs, 1 H, N*H*), 3.90 (bt, J = 5.3 Hz, PhCH=CHC*H*$_2$NH), 1.46 (s, 9 H, COOC(C*H*$_3$)$_3$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 155.69 (*C*OOC(CH$_3$)$_3$), 136.61, 131.21, 128.43, 127.44, 126.30, 126.23, 79.29 (*C*H$_2$NH), 42.63 (COO*C*(CH$_3$)$_3$), 28.32 (COOC(*C*H$_3$)$_3$); IR (neat) 3190, 1690 cm^{-1}; mass spectrum (CI), *m/z* (rel intensity) 233 (2, M$^+$), 177 (64, M$^+$ − C$_4$H$_8$), 132 (38, M$^+$ − C$_4$H$_8$ − CO$_2$), 116 (100).

Anal. Calcd for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21. Found: C, 72.31; H, 7.95.

1-Amino-2(*E*),4(*E*)-hexadiene (8h). Into a 25-mL round-bottom flask equipped with a magnetic stirrer were added **7h** (0.217 g, 1.09 mmol) and ethyl ether (12 mL). Trifluoroacetic acid (0.248 g, 2.18 mmol) and concentrated HCl (5.0 μL) were added, and the solution was stirred at 23 °C for 30 h. The yellow-orange solution was poured into ether (30 mL) and extracted with saturated aqueous $NaHSO_4$ (4 × 10 mL). The aqueous portion was made basic by the addition of a cold, saturated solution of aqueous Na_2CO_3 and extracted with methylene chloride (6 × 20 mL). The organic portion was dried ($MgSO_4$) and concentrated in vacuo to provide 0.085 g (80%) of **8h** as a yellow oil with spectral properties consistent with those reported earlier.[8]

Acknowledgment. We thank the American Scandinavian Foundation and the Upjohn Company for Fellowships for R.D.C. We thank the Zahm Fund (University of Notre Dame) for providing travel expenses, the Johnson Matthey Inc. for loaning palladium compounds to us, and Professor Ragnarsson for his donation of a sample of **2**. This research was supported by grants from the National Institutes of Health (U.S.A.) and the Natural Science Research Council (Sweden).

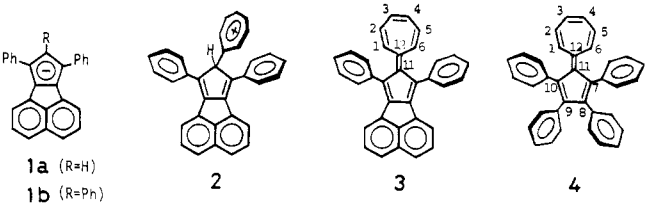
Synthesis of 7,9-Diphenyl-8-tropyliumyl-8*H*-cyclopent[*a*]acenaphthylene Cation Having an Intramolecular Charge-Transfer Interaction and Its Transformation into the Sesquifulvalene Derivative

Koichi Komatsu,* Ryuji Fujiura, and Kunio Okamoto[1]

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan

Received January 25, 1988

During the course of our study of phenyl-substituted cyclopent[*a*]acenaphthylenide ions **1a,b**,[2] reactivities toward various stable carbocations were investigated. This



1a (R=H) **1b** (R=Ph) **2** **3** **4**

note describes the syntheses and properties of the title cation **2**, obtained through the reaction of **1a** with tropylium ion ($C_7H_7^+$), and of the related sesquifulvalene derivative **3**. Although **3** can be looked upon as a homologue of the known sesquifulvalene **4**,[3] replacement of the two phenyl groups with a 1,8-naphthylene unit has been found

(1) Present address: Meisei Chemical Works, Ltd., 1 Nakazawacho, Nishikyogoku, Ukyo-ku, Kyoto 615, Japan.
(2) Komatsu, K.; Fujiura, R.; Okamoto, K. *Chem. Lett.* **1988**, 265.
(3) Prinzbach, H.; Seip, D.; Knothe, L.; Faisst, W. *Justus Liebigs Ann. Chem.* **1966**, *698*, 34.

0022-3263/88/1953-3849$01.50/0