Experimental Section

Materials. The arylthallium bis(trifluoroacetates) were prepared by established procedures.[11] Thallium and thallium compounds are extremely toxic and should be handled with utmost care.[10] Thallium trifluoroacetate (94%) was obtained from Aldrich Chemical Co. and was used without further purification. THF was stored at reflux with sodium metal and benzophenone in a recycling solvent still. Li_2PdCl_4 was prepared by dissolving $PdCl_2$ and LiCl in water (heating is required), evaporating the water, and heating in vacuo at 100 °C until a red-purple solid was obtained.

Identification of Coupling Products. All of the biaryls that were prepared have been previously reported. They were identified by IR (Perkin Elmer 700) and ^1H NMR (Varian EM360) spectroscopy and melting points (uncorrected).

General Coupling Procedure. To 2.00 mmol of thallated aromatic dissolved in 10 mL of THF in a flask equipped with a magnetic stirrer was added 0.20 mmol (52 mg) of Li_2PdCl_4. The mixture was either left at 25 °C for 5 days or refluxed for 5 h. Both methods worked equally well. Evaporation of the THF was followed by the addition of 5 mL of water and extraction with three 5-mL portions of hexane unless otherwise noted below. The combined organic layers were dried (Na_2SO_4), and the volume was reduced to 2 mL by evaporation. All of the products were further purified by filtration through 0.5–8 g of silica gel followed by recrystallization. Product **2e** required column chromatography (see below).

4,4'-Dimethoxybiphenyl (2e). Following the general procedure, 1.07 g (2.00 mmol) of thallated anisole (this consisted of **1e** contaminated with 7% of the ortho isomer), 52 mg (0.20 mmol) of Li_2PdCl_4, and 10 mL of THF were refluxed 5 h. Workup with chloroform instead of hexane was followed by column chromatography on 25 g of silica gel with chloroform as the eluent. Elution proceeded as follows: 50 mL, nil; 150 mL, 191 mg (89% based on crude thallated anisole, 96% based on **1e**) of **2e** as a white crystalline solid with spectral properties in agreement with those reported. Recrystallization from ether gave essentially all of the material back as white flakes: mp 173–175 °C (lit. mp 176–178 °C).

4,4'-Bis(3-carboxypropyl)biphenyl (2f). To a slurry of 0.959 g (2.00 mmol) of thallated 4-phenylbutyric acid[13] and 10 mL of THF in a flask equipped with a magnetic stirrer was added 170 μL (2.2 mmol) of trifluoroacetic acid to give a homogeneous solution of **1f**. Addition of 52 mg (0.20 mmol) of Li_2PdCl_4 was followed by refluxing for 5 h. Most of the solvent was then removed by rotary evaporation. The resulting material was treated with 5 mL of 10% HCl and was washed with three 10-mL portions of ethyl acetate. Drying was achieved by evaporating the ethyl acetate, dissolving in 10 mL of methanol, and adding Na_2SO_4. The methanol solution was then filtered through 1 g of silica gel to remove residual thallium salts. Part of the solvent was then evaporated so that **2e** would crystallize when cooled in an ice/NaCl bath. The white crystalline product was collected and extensively dried in an Abderhalden containing P_2O_5. This resulted in 293 mg (90%) of **2f**: IR (Nujol mull) 2500–3500, 1685, 940 cm^{-1}; ^1H NMR (acetone-d_6) δ 1.9 (m, 4 H), 2.33 (t, 4 H), 2.65 (t, 4 H), 7.27 (d, J = 8 Hz, 4 H), 7.53, (d, J = 8 Hz, 4 H); mp 170–174 °C (lit.[14] mp 185 °C).

Acknowledgment. Financial assistance from FHSU through the Graduate Council Research Committee is gratefully acknowledged.

Registry No. **1a**, 23586-54-1; **1b**, 23586-55-2; **1c**, 67106-45-0; **1d**, 38579-34-9; **1e**, 28688-23-5; **1f**, 33930-55-1; **1g**, 23586-56-3; **1h**, 77212-88-5; **1i**, 23586-58-5; **2a**, 92-52-4; **2b**, 613-33-2; **2c**, 7641-81-8; **2d**, 1625-91-8; **2e**, 2132-80-1; **2f**, 6918-69-0; **2g**, 4920-95-0; **2h**, 4920-94-9; **2i**, 2050-68-2; Li_2PdCl_4, 15525-45-8.

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[13] The recrystallized product obtained in the thallation of 4-phenylbutyric acid is the mono(trifluoroacetate) rather than the bis(trifluoroacetate) (see ref 11b). It is completely insoluble in THF. Dissolution occurs within about 1 min when 1 molar equiv of trifluoroacetic acid is added.

[14] (a) Gildersleve, D. R.; Tute, M. S. Belg. Pat. 670 862; *Chem. Abstr.* **1966**, *65*, 8827f. (b) Diekmann, H.; Chang, C. K.; Traylor, T. G. *J. Am. Chem. Soc.* **1971**, *93*, 4068–4070.

Synthesis of Imines of α,β-Acetylenic Ketones

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In order to extend our earlier studies of the photochemical behavior of imines of α,β-ethylenic ketones,[2] we were interested in preparation of simple aliphatic imines of α,β-acetylenic ketones. We found no report in the literature concerning these compounds[3] and have now developed an exchange procedure that should be generally useful for their preparation from the corresponding alkyl alkynyl ketones.

As expected, attempts to react acetylenic ketones directly with primary amines gave enamino ketones as major products. Minor amounts of the desired imine were isolated when molecular sieves were employed. Thus, 3-pentyn-2-one (**1a**)[4] and methylamine yielded 54% of **2** and only 5–15% of the ynimine **3** (Chart I). However, reasonable yields of ynimines **4a** and **4b** were obtained by the reaction of **1a** and **1b**[5] with *N*-ethylidenecyclohexanamine (**5**)[6] at 25 °C and 100 torr for 20 h. This method is superior to one previously described[7] for saturated imines that uses isopropylideneamines and zinc chloride as a catalyst. With the aldimine **5** the reaction proceeds at room temperature and no catalyst is needed. The exchange is driven by continuous removal at low pressure of the acetaldehyde formed. These acetylenic imines could be fully characterized but were rather unstable on storage. *N*-Methyl imine **3** decomposed slowly even at −30 °C.

Since we had previously shown that α-fluorine substituents increase the reactivity of excited imines in cycloaddition reactions,[2,8] we were also interested in preparing imines of alkynyl perfluoroalkyl ketones. These ketones have not been generally accessible, but we found that **1c,d** could be conveniently prepared from the corresponding perfluorocarboxylic acid and an excess of the Grignard–acetylide.[9] Unfortunately these fluorinated ketones reacted with **5** to afford only minor amounts of acetylenic imines, as monitored by infrared spectroscopy; attempts to isolate these ynimines were unsuccessful.

Experimental Section

The following spectrometers were used: IR, Perkin-Elmer 297; UV, PE 200; ^1H NMR, Bruker WH-270 (270 MHz); ^{13}C NMR, Varian WP-80; mass spectrum, Varian CH7. Chemical shifts are reported in parts per million relative to internal Me_4Si. All boiling points are uncorrected. Elemental analyses were obtained in the analytical laboratory at the University of Hamburg.

3-Pentyn-2-ylidenemethanamine (3). Methylamine [prepared from methylammonium chloride (0.3 mol)] was added to

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[1] The Rockefeller University, New York, NY.

[2] Margaretha, P. *Helv. Chim. Acta* **1978**, *61*, 1025.

[3] During the course of this work preparation of a single α,β-ynimine was reported in connection with a novel synthesis of ketones by way of imines: Marks, M. J.; Walborsky, H. M. *J. Org. Chem.* **1982**, *47*, 52.

[4] Braude, E. A.; Jones, E. R. H.; Sondheimer, F.; Toogood, J. B. *J. Chem. Soc.* **1949**, 607.

[5] Wilson, J. W.; Stubblefield, V. S. *J. Am. Chem. Soc.* **1969**, *90*, 3423.

[6] Beekunis, G. E.; Thoma, J. A. Ger. Offen. 2 109 267: *Chem. Abstr.* **1971**, *75*, 140353.

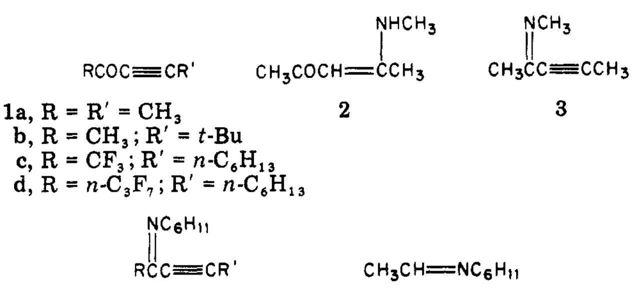
[7] Haury, V. E. U. S. Pat. 2 692 284; *Chem. Abstr.* **1955**, *49*, 15946.

[8] Margaretha, P. *Helv. Chim. Acta* **1982**, *65*, 290.

[9] This general method has been used for synthesis of alkyl perfluoroalkyl ketones: Dishart, K.; Levine, R. *J. Am. Chem. Soc.* **1956**, *78*, 2268.

0022-3263/83/1948-1925$01.50/0

Chart I[a]



$RCOC{\equiv}CR'$

1a, R = R' = CH_3
b, R = CH_3; R' = *t*-Bu
c, R = CF_3; R' = *n*-C_6H_{13}
d, R = *n*-C_3F_7; R' = *n*-C_6H_{13}

$CH_3COCH{=}C(NHCH_3)CH_3$

2

$CH_3C({=}NCH_3)C{\equiv}CCH_3$

3

$RC({=}NC_6H_{11})C{\equiv}CR'$

4

$CH_3CH{=}NC_6H_{11}$

5

[a] C_6H_{11} = cyclohexyl.

1a (8.2 g, 0.1 mol) and 4-Å molecular sieves (10 g) at −10 °C by using a condenser cooled to −30 °C, the reaction temperature rising to 15 °C. After 0.5 h the mixture was distilled, affording **3** [0.5–1.4 g (5–15%); bp 65–70 °C (150 mm); IR (neat) 2220, 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.28 (s, 3 H), 2.10 (s, 3 H), 2.03 (s, 3 H); slow decomposition even at −30 °C] and **2**: 6.1 g (54%); bp 88 °C (12 mm).[10]

Reaction of Ketones 1a,b with Ethylidenecyclohexanamine (5). Equimolar amounts of **1a** or **1b** and **5**[6] (0.05 mol) were stirred at 25 °C under reduced pressure (100 mm) for 20 h. Subsequent distillation afforded ynimines **4a** and **4b**.

Data for 4a: 42%; bp 90–108 °C (15 mm); IR (neat) 2210, 1610 cm^{-1}; UV (C_6H_{12}) 218 nm (log ϵ 3.80), 259 sh (2.51); ^1H NMR ($CDCl_3$) δ 3.6 (m, 1 H), 2.12 (s, 3 H), 2.03 (s, 3 H), 2.1–1.05 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 147.74, 92.78, 74.93, 63.91, 33.53, 33.52, 25.78, 24.95, 24.94, 4.06; MS (70 eV), *m/z* (relative intensity) 163 (26, M$^+$), 120 (100). Anal. Calcd for $C_{11}H_{17}N$: C, 80.92; H, 10.50; N, 8.58. Found: C, 80.33; H, 10.72; N, 8.85.

Data for 4b: 42%; bp 105–107 °C (10 mm); IR (neat) 2200, 1610 cm^{-1}; UV (C_6H_{12}) 220 nm (log ϵ 4.04), 270 (2.45); ^1H NMR (CCl_4) δ 3.4 (m, 1 H), 2.00 (s, 3 H), 2.0–1.2 (m, 10 H), 1.30 (s, 9 H); ^{13}C NMR (C_6D_6) δ 147.24, 104.83, 74.95, 64.26, 34.93, 34.02, 30.78, 27.86, 26.38, 25.27; MS (70 eV), *m/z* (relative intensity) 205 (8, M$^+$), 190 (100). Anal. Calcd for $C_{14}H_{23}N$: C, 81.89; H, 11.29; N, 6.82. Found: C, 81.71; H, 11.37; N, 7.08.

1,1,1-Trifluoro-3-decyn-2-one (1c). Trifluoroacetic acid (35.4 g, 0.31 mol) in 50 mL of dry ether was added dropwise to a solution of 1-octynylmagnesium bromide (0.09 mol) in 200 mL ether. After the reaction mixture was heated to reflux for 2 h and allowed to stand overnight at 25 °C, a mixture of 400 g of ice and 100 mL of HCl was added, the organic phase was separated, and the aqueous phase was saturated with NaCl and extracted with ether (4×). The combined organic phases were washed with saturated $NaHCO_3$ and NaCl solutions and dried over Na_2SO_4. The ether was removed by distillation through a 40-cm Vigreux column and the residue distilled at reduced pressure to afford **1c**: 28.1 g (44%); bp 65–68 °C (15 mm); IR (neat) 2200, 1705 cm^{-1}; UV (C_6H_{12}) 230 nm (log ϵ 3.93), 237 sh (3.88), 312 (1.26): ^1H NMR ($CDCl_3$) δ 2.50 (t, 2 H), 1.80–1.65 (m, 2 H), 1.57–1.20 (m, 6 H), 0.9 (t, 3 H); ^{13}C NMR (CD_3OD) δ 167.07, 122.94, 89.65, 73.58, 31.21, 28.53, 27.28, 22.51, 19.49, 13.92; MS (70 eV), *m/z* (relative intensity) 191 (2.1, M$^+$ − CH_3), 137 (100). Anal. Calcd for $C_{10}H_{13}F_3O$: C, 58.25; H, 6.35. Found: C, 58.36; H, 6.28.

1,1,1,2,2,3,3-Heptafluoro-5-dodecyn-4-one (1d). Prepared as above from perfluorobutanoic acid and 1-octynylmagnesium bromide: 27% yield; bp 80–82 °C (10 mm); IR (neat) 2210, 1705, 1210 cm^{-1}; UV (C_6H_{12}) 234 nm (log ϵ 4.03), 242 sh (3.97), 317 (1.61); ^1H NMR ($CDCl_3$) δ 2.5 (t, 2 H), 1.8–1.65 (m, 2 H), 1.6–1.2 (m, 6 H), 0.9 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 168.95 (t), 138–94 (m, 3 CF), 106.27, 73.51, 31.19, 28.49, 27.26, 22.47, 19.55, 13.67; MS (70 eV), *m/z* (relative intensity) 291 (0.7, M$^+$ − CH_3), 137 (100). Anal. Calcd for $C_{12}H_{13}F_7O$: C, 47.07; H, 4.28. Found C, 47.18; H, 4.36.

Acknowledgment. Financial support for this research was provided by NATO (Research Grant 107.81), by Deutsche Forschungsgemeinschaft, by the Konrad-Adenauer-Stiftung through a fellowship to C.S., and by the Fonds der Chemischen Industrie.

Registry No. **1a**, 7299-55-0; **1b**, 10564-81-5; **1c**, 85336-10-3; **1d**, 85336-11-4; **3**, 85336-12-5; **4a**, 85336-13-6; **4b**, 85336-14-7; **5**, 1193-93-7; 1-octynyl bromide, 38761-67-0; heptafluorobutanoic acid, 375-22-4; methylamine, 74-89-5; trifluoroacetic acid, 76-05-1.

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The Fate of 2-Homoadamantyl Carbene

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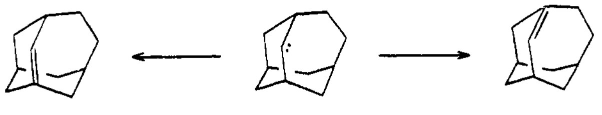
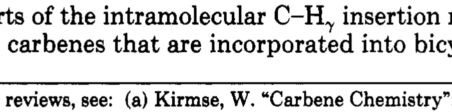
Intramolecular carbene insertion reactions have provided the means for the synthesis of many highly strained polycyclic hydrocarbons.[1] Of particular interest are the fates of carbenes that have multiple avenues of reaction available to them. A case in point is 2-homoadamantyl carbene (1). Although olefin formation from 1 is not expected to be significant, since insertion into the C–H bonds adjacent to C-2 in 1 can only provide the anti-Bredt alkenes 2 and 3, alternative C–H bond insertions in 1 could lead to the five "non-bridgehead" dehydrohomoadamantanes 4–8 (Scheme I).[2,3] In view of this, we have undertaken an examination of the behavior of this species.



It is now well established that free carbenes can be generated by the thermal decomposition of the dry alkali salts of tosylhydrazones.[1] Consequently, 2-homoadamantyl carbene was prepared by pyrolysis of the dry lithium salt of the *p*-toluenesulfonylhydrazone of 2-homoadamantanone (9) at 190–220 °C for 1 h, according to the general procedure of Friedman and Shechter.[4] This reaction gives 4 as the sole volatile product in 40% yield. The identity of 4 was established by comparison of its spectral data with those of an authentic sample prepared by an alternative route.[2a]



Reports of the intramolecular C–H_γ insertion reactions of other carbenes that are incorporated into bicyclic and

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(1) For reviews, see: (a) Kirmse, W. "Carbene Chemistry"; Academic Press: New York, 1971; pp 236–260. (b) Baron, W. J.; Decamp, M. R.; Hendrick, M. E.; Jones, M., Jr.; Levin, R. H.; Sohn, M. B. In "Carbenes"; Jones, M., Jr., Moss, R. A., Ed.; Wiley-Interscience: New York, 1973; Chapter 1. (c) Casanova, J.; Waegell, B. *Bull. Soc. Chim. Fr.* **1975**, 922–932. (d) Shapiro, R. H. *Org. React.* **1976**, *23*, 405–507.

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(3) The formation of four-membered rings in such reactions is unusual.[1]

(4) Friedman, L.; Shechter, H. *J. Am. Chem. Soc.* **1959**, *81*, 5512–5513.