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$_6$H$_{13}$
 d, R = n-C$_3$F$_7$; R' = n-C$_6$H$_{13}$
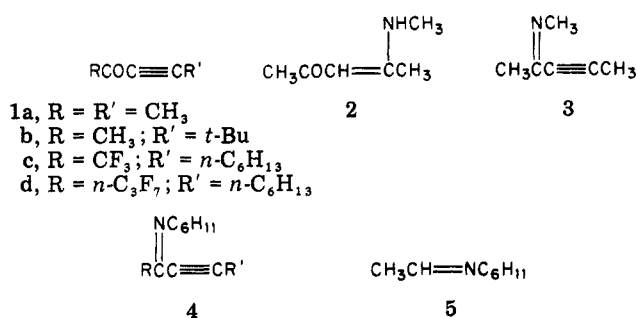
2   3

4   5

[a] C$_6$H$_{11}$ = 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}; ^{1}H 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 Ethylidenecyclohexan-amine (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$_6$H$_{12}$) 218 nm (log ε 3.80), 259 sh (2.51); ^{1}H 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$_6$H$_{12}$) 220 nm (log ε 4.04), 270 (2.45); ^{1}H 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$_6$D$_6$) 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$_2$SO$_4$. 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$_6$H$_{12}$) 230 nm (log ε 3.93), 237 sh (3.88), 312 (1.26): ^{1}H 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$_3$OD) 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$_3$O: 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$_6$H$_{12}$) 234 nm (log ε 4.03), 242 sh (3.97), 317 (1.61); ^{1}H 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$_7$O: C, 47.07; H, 4.28. Found C, 47.18; H, 4.36.

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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

2   1   3
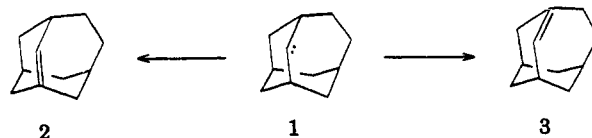
be significant, since insertion into the C–H bonds adjacent to C-2 in 1 can only provide the anti-Bredt alkenes 2 and 3, alternative C–H bond insertions in 1 could lead to the five "non-bridgehead" dehydrohomoadamantanes 4–8 (Scheme I).[2,3] In view of this, we have undertaken an examination of the behavior 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-homo-adamantanone (9) at 190–220 °C for 1 h, according to the

9   4
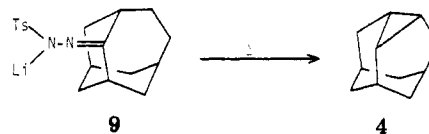
general procedure of Friedman and Shechter.[4] This reaction gives 4 as the sole volatile product in 40% yield. The identity of 4 was established by comparison of its spectral data with those of an authentic sample prepared by an alternative route.[2a]

Reports of the intramolecular C–H$_\gamma$ 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.

(2) With the exception of 7, all of these hydrocarbons are known. (a) 4: Majerski, Z.; Liggero, S. H.; Schleyer, P. v. R. *J. Chem. Soc. D* 1970, 949–950. Yamaguchi, R.; Katsushima, T.; Kawanisi, M. *Bull. Chem. Soc. Jpn.* 1974, 47, 2830–2835. (b) 5: Sasaki, T.; Eguchi, S.; Hirako, Y. *J. Org. Chem.* 1977, 42, 2981–2985. Katsushima, T.; Yoshikawa, M.; Yamaguchi, R.; Kawanisi, M. *Bull. Chem. Soc. Jpn.* 1980, 53, 2618–2620. (c) 6: Murray, R. K., Jr.; Goff, D. L.; Ratych, R. E. *Tetrahedron Lett.* 1975, 763–764. (d) 8: Murray, R. K., Jr.; Ford, T. M. *J. Org. Chem.* 1979, 44, 3504–3508. Katsushima, T.; Maki, K.; Yamaguchi, R.; Kawanisi, M. *Bull. Chem. Soc. Jpn.* 1980, 53, 2031–2035.

(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.

(10) Holtzclow, H. F., Jr.; Collman, J. P.; Alire, R. M. *J. Am. Chem. Soc.* 1958, 80, 1100.

Scheme I
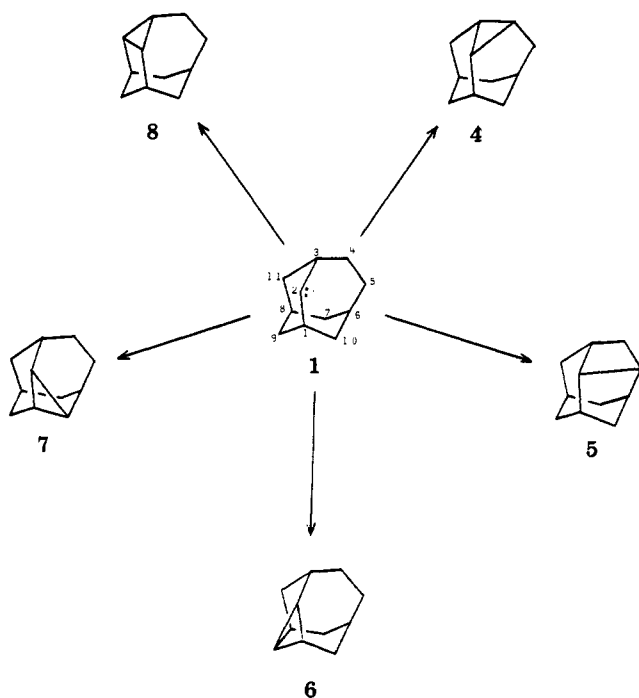
polycyclic hydrocarbons suggest that such reactions occur exclusively or preferentially by insertion of the carbene into the C–H$_\gamma$ bond nearest to it that comes closest to being coplanar with the nonbonded orbitals of the carbene.[5,6] If this generalization holds for 2-homoadamantyl carbene, then examination of a molecular model of **1** clearly shows that the nonbonded orbitals at C-2 can only be coplanar with the C$_4$–H bond endo to it if the two-carbon bridge in **1** is twisted. Moreover, manipulation of the molecular model indicates that if the two-carbon bridge in **1** is not twisted, then the highest degree of overlap of the non-bonded orbitals at C-2 would be with the C$_9$–H bond endo to it. Next best would be the C$_{10}$–H endo bond. Thus, if the hydrogens in the two-carbon bridge of **1** were eclipsed or nearly eclipsed, the reaction products of **1** would have been expected to be **6** and/or **7**.

Experimental Section

2-Homoadamantanone Tosylhydrazone (13). Equimolar quantities of 2-homoadamantanone[8] (0.387 g, 2.36 mmol) and *p*-toluenesulfonylhydrazine (0.440 g, 2.36 mmol) were dissolved in methanol (5 mL). The stirred solution was brought to a gentle boil and refluxed for 2 h. After slow cooling to room temperature, the reaction mixture was stored overnight at 0 °C. The resulting white solid was filtered, washed with cold methanol, and dried in vacuo to give 0.416 g (53% yield) of **13**: mp 137.5–139.5 °C; ^{1}H NMR δ (CDCl$_3$) 8.1–7.3 (4 H, d of d, aromatic hydrogens) and 3.3–0.9 (20 H, complex m containing CH$_3$ signal at δ 2.45).

Anal. Calcd for C$_{18}$H$_{24}$N$_2$O$_2$S: C, 65.03; H, 7.28. Found: C, 64.93; H, 7.24.

2,4-Dehydrohomoadamantane (4). *n*-Butyllithium (0.7 mL of a solution 2.4 M in hexane) was slowly added to a stirred solution of **13** (0.352 g, 1.06 mmol) in 5 mL of tetrahydrofuran

(5) In addition to the examples cited in ref 1, see: (a) Skare, D.; Majerski, Z. *J. Chem. Soc., Chem. Commun.* **1974**, 1000–1001. (b) Casanova, J.; Waegell, B.; Koukoua, G.; Toure, V. *J. Org. Chem.* **1979**, *44*, 3976–3979. (c) Majerski, Z.; Djigas, S.; Vinkovic, V. *Ibid.* **1979**, *44*, 4064–4069. (d) Hirsl-Starcevic, S.; Majerski, Z. *Ibid.* **1982**, *47*, 2520–2525.

(6) In more complex cases the course of intramolecular C–H$_\gamma$ insertion reactions may depend on the nucleophilicity and the type (tertiary, secondary, or primary) of the C–H$_\gamma$ bonds that are available.[7]

(7) See ref 5d and references cited therein.

(8) Murray, R. K., Jr.; Babiak, K. A.; Morgan, T. K., Jr. *J. Org. Chem.* **1975**, *40*, 2463–2468.

(freshly distilled from lithium aluminum hydride) at 0 °C under nitrogen. The resulting pale yellow solution was stirred at 0 °C for 2 h and then at 25 °C for 1 h. At this point the solvent was evaporated at reduced pressure, and the residue was dried at 60 °C (0.01 mm) for 0.5 h. The reaction flask was then connected to an all-glass pyrolysis apparatus leading to a trap maintained at –78 °C. The lithium salt of **13** was heated to 190 °C at 0.1 mm with an oil bath, and it was kept at this temperature for 30 min. Subsequently, the reaction mixture was heated to 220 °C at 0.1 mm for a further 30 min. Analysis of the distillate by GLC (10 ft × 0.25 in. SE-30 column, 130 °C) indicated a single product. Isolation of this compound by GLC (above conditions) gave pure **4**, which was identified by comparison of its ^{1}H NMR, ^{13}C NMR, and IR spectra with those of an authentic sample of **4** prepared by an alternative route.[4a] GLC analysis of the distillate showed that **4** was obtained in ca. 40% yield.

Selective Preparation. 38. A Convenient Preparation of 2-(Acylamino)biphenyls and *N*-Acetylaniline Derivatives Using the *tert*-Butyl Group as a Positional Protective Function[1]

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Recently, we reported that[2] many kinds of aromatic compounds can be selectively prepared by using the *tert*-butyl function as a positional protective group.

We now report a convenient preparation of 2-(acetyl-amino)biphenyl (**7a**) and 2-(benzoylamino)biphenyl (**7b**), *N*-acetyl-*o*-toluidine (**18**), and *N*-acetyl-2,6-dimethylaniline (**24**) from biphenyl (**1**), toluene (**13**) and *m*-xylene (**19**), respectively, in five steps by using the *tert*-butyl blocking group (see Scheme I).

The preparations of 4,4′-di-*tert*-butyl- (**3**),[3] 2-nitro-4,4′-di-*tert*-butyl- (**4**)[4] and 2-amino-4,4′-di-*tert*-butylbi-phenyl (**5**)[4] were described in previous papers. Acylation of **5** with acetic anhydride and benzoyl chloride affords the corresponding *N*-acyl derivatives **6a** and **6b** in 83% and 96% yields, respectively.

Although it has been reported that heating 2,6-di-*tert*-butyl-4-piperidinophenol (**9**) in 85% phosphoric acid affords 4-piperidinophenol (**10**),[5] the similar reaction as well as the aluminum chloride nitromethane catalyzed trans-alkylation of **5** gives only 2-amino-4-*tert*-butylbiphenyl (**11**) and not the expected 2-aminobiphenyl (**12**) (see Scheme II).

However, the aluminum chloride catalyzed trans-*tert*-butylation of both **6a** and **6b** in benzene affords the corresponding *N*-acyl derivatives **7a** and **7b** in good yields. This method seems to be widely applicable to the selective preparation of ortho-substituted aniline derivatives. In-

(1) Part 37. Tashiro, M.; Yoshiya, H.; Fukata, G. *J. Org. Chem.* **1982**, 4425.

(2) Tashiro, M. *Synthesis* **1979**, 921.

(3) Tashiro, M.; Yamato, T. *Org. Prep. Proced. Int.* **1978**, *10*, 143.

(4) Tashiro, M.; Yamato, T. *J. Org. Chem.* **1979**, *44*, 3037. In this report, the melting point of **11** has been reported as 110–112 °C, however, it is misrecorded one. The correct melting point is 80–82 °C.

(5) Tashiro, M.; Fukata, G. *Synthesis* **1979**, 602.

(6) Tashiro, M.; Fukata, G.; Yamato, T. *Org. Prep. Proced. Int.* **1976**, 263.