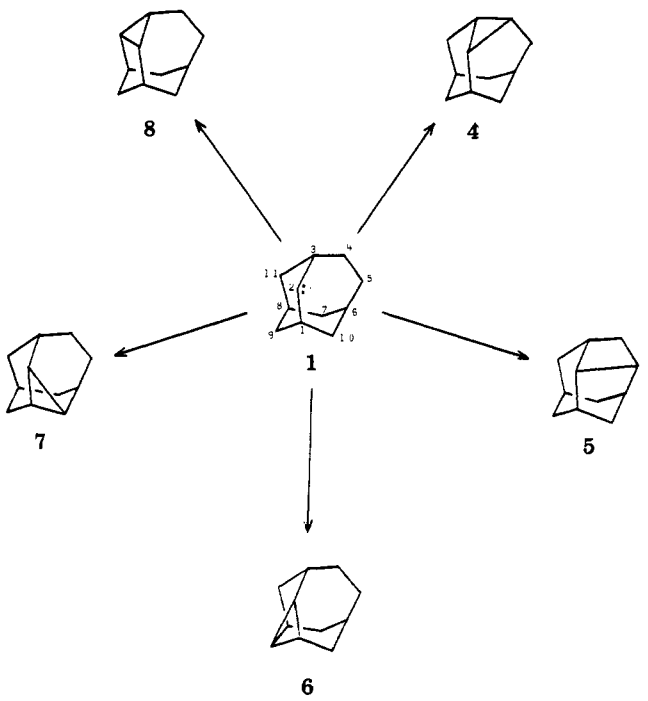
Scheme I



polycyclic hydrocarbons suggest that such reactions occur exclusively or preferentially by insertion of the carbene into the C–H_γ 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 nonbonded 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 $C_{18}H_{24}N_2O_2S$: 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 (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.

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Registry No. **1**, 85337-06-0; **4**, 28786-66-5; **9**, 85337-07-1; **13**, 85337-08-2; 2-homoadamantanone, 61494-94-8.

(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_γ insertion reactions may depend on the nucleophilicity and the type (tertiary, secondary, or primary) of the C–H_γ 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.

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-(acetylamino)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*-butylbiphenyl (**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 transalkylation 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.

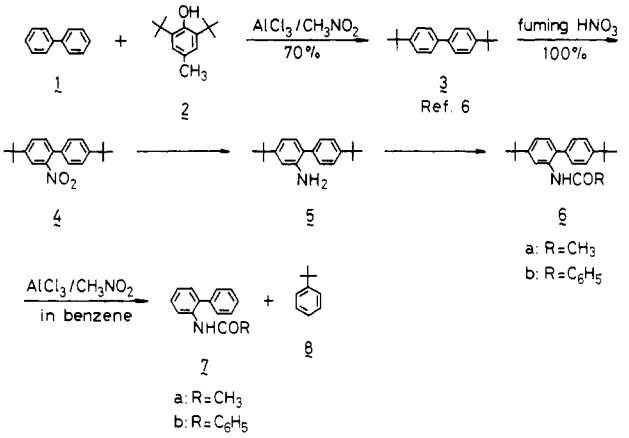
(4) Tashiro, M.; Yamato, T. *J. Org. Chem.* **1979**, *44*, 3037. In this report, the melting point of **11** has been reported as 110–112 °C, however, it is misrecorded one. The correct melting point is 80–82 °C.

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

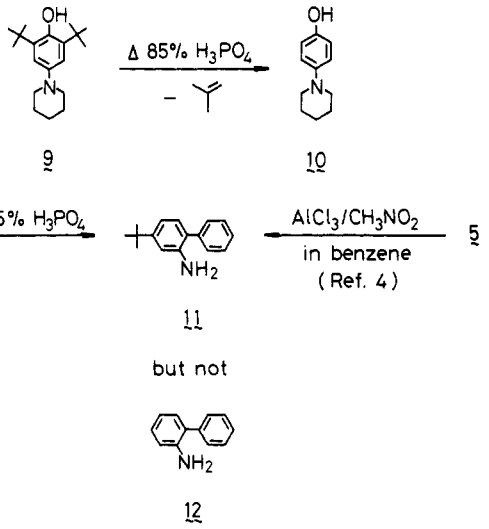
(6) Tashiro, M.; Fukata, G.; Yamato, T. *Org. Prep. Proced. Int.* **1976**, 263.

0022-3263/83/1948-1927$01.50/0

Scheme I



Scheme II



deed, *N*-acetyl-*o*-toluidine (**18**) and *N*-acetyl-2,6-dimethylaniline (**24**) were prepared from toluene (**13**) and *m*-xylene (**19**), respectively (see Scheme III).

Experimental Section

Transalkylation of 6a in Benzene. After a mixture of 200 mg (0.6 mmol) of **6a**, 300 mg (2 mmol) of aluminum chloride, and 6 mL of benzene is stirred at room temperature for 3 h, it is quenched with water and extracted with ether. The ether solution is washed with water, dried with sodium sulfate, and evaporated in vacuo to leave the residue, which was recrystallized from hexane to give 102 mg (79%) of **7a**: mp 123–124 °C; lit.[7] mp 120 °C.

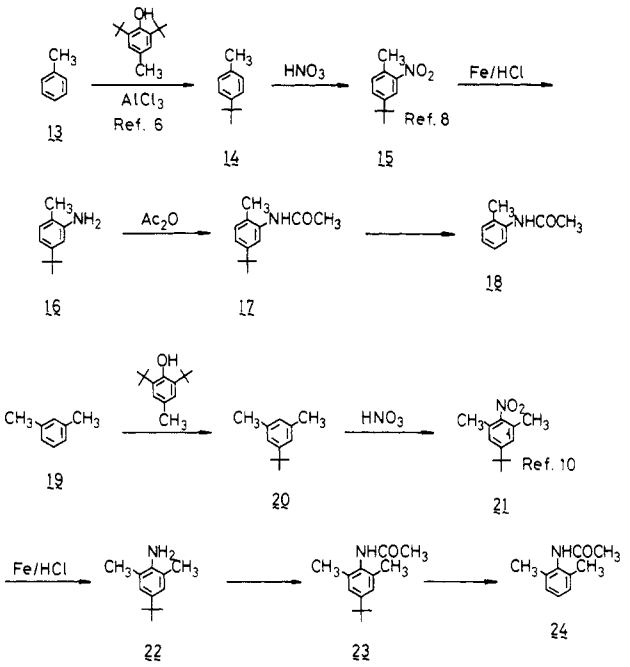
Transalkylation of 6b in Benzene. A mixture of 500 mg of **6b**, 550 mg (3.6 mmol) of aluminum chloride, and 15 mL of benzene is treated and worked up as described above to give 222 mg (63%) of **7b**: colorless needles, mp 88–89 °C (hexane). Anal. Calcd for $C_{19}H_{16}NO$: C, 83.49; H, 5.53; N, 5.13. Found: C, 83.50; H, 5.60; N, 5.43.

Treatment of 5 with Refluxing 85% Phosphoric Acid. After a mixture of 200 mg of **5** and 6 mL of phosphoric acid is heated at 220 °C for 24 h, it is poured into a large amount of water, made basic to litmus with 10% sodium hydroxide, and extracted with ether. The ether solution is washed with water, dried with sodium sulfate, and evaporated in vacuo to leave the residue, which is chromatographed on silica gel with benzene as an eluent to give 120 mg (100%) of **11**: colorless needles (ethanol–water), mp 80–82 °C; lit.[4] mp 110–112 °C.

Transalkylation of 17 in Benzene. A mixture of 2.05 g (10 mmol) of **17**, 5.28 g (40 mmol) of aluminum chloride, and 100 mL of benzene is treated and worked up as described above to give 800 mg (54%) of **18**: colorless needles (hexane–benzene, 2:1); mp 109–110 °C, lit.[9] mp 110 °C.

(7) Sako, S. *Bull. Chem. Soc. Jpn.* **1934**, *6*, 54.
(8) Carpenter, M. S.; Easter, W. M.; Wood, T. F. *J. Org. Chem.* **1951**, *16*, 586.

Scheme III



Transalkylation of 23 in Benzene. A mixture of 2.19 g (10 mmol) of **23**, 5.28 g (40 mmol) of aluminum chloride, and 100 mL of benzene is treated and worked up as described above to give 1.33 g (82%) of **24**: colorless needles, mp 176–177 °C (hexane–benzene, 1:1), lit.[11] mp 177 °C.

Compounds **6a**, **6b**, **17**, and **23** were prepared in the usual manner.

6a: colorless needles, mp 136–138 °C (hexane). Anal. Calcd for $C_{22}H_{29}NO$: C, 81.69; H, 9.04; N, 4.33. Found: C, 81.60; H, 9.15; N, 4.21.

6b: colorless prisms, mp 146 °C. Anal. Calcd for $C_{27}H_{31}NO$: C, 84.11; H, 8.11; N, 3.63. Found: C, 84.31; H, 8.06; N, 3.63.

17: colorless needles, mp 97–98 °C (hexane). Anal. Calcd for $C_{18}H_{19}NO$: C, 76.05; H, 9.32; N, 6.82. Found: C, 76.05; H, 9.69; N, 6.95.

23: colorless needles, mp 156–157 °C (hexane–benzene, 5:1). Anal. Calcd for $C_{14}H_{21}NO$: C, 76.67; H, 9.65, N, 6.39. Found: C, 77.10; H, 9.81; N, 6.59.

Registry No. **2**, 128-37-0; **5**, 70728-92-6; **6a**, 85336-15-8; **6b**, 85336-16-9; **7a**, 2113-47-5; **7b**, 7404-97-9; **8**, 98-06-6; **11**, 70729-04-3; **13**, 108-88-3; **14**, 98-51-1; **15**, 62559-08-4; **16**, 85336-17-0; **17**, 85336-18-1; **18**, 6830-82-6; **19**, 108-38-3; **20**, 98-19-1; **21**, 6279-89-6; **22**, 42014-60-8; **23**, 85336-19-2; **24**, 2198-53-0; benzene, 71-43-2.

(9) Kaufmann, A. *Ber.* **1909**, *42*, 3481.
(10) Carpenter, M. S.; Easter, W. M. *J. Org. Chem.* **1954**, *19*, 77.
(11) Busch, M. *Ber.* **1899**, *32*, 1008.

Reaction of Acrylonitrile with Benzophenone via the Derived Vinyl Carbanion

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Vinyl carbanion intermediates are formed in acid–base-type reactions of activated olefins of the type Y—

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