The mixture was extracted with 40 mL of saturated aqueous $NaHCO_3$ solution, the organic layer dried over anhydrous $MgSO_4$, and the spent drying agent removed by filtration. Evaporation of the solvent from the filtrate left 8.54 g of a yellow semisolid. Analysis by NMR ($CDCl_3$) indicated that this was a mixture of approximately 75% dimethyl fumarate (**5**; signal at $\delta$ 6.78) and 25% of a 60:40 mixture of **1a** and **2a** (signals at $\delta$ 5.45 and 6.30, respectively). Although no rigorous attempt was made to separate the components, preparative layer chromatography ($CHCl_3$) provided white crystals (mp 102.5–104 °C) which were identical in all respects with dimethyl fumarate (mixture melting point 102–104.5 °C), thus confirming the assignment made by NMR of the crude mixture.

**Eliminations via 7d, 9b, and 9d.** These reactions were conducted identically. A solution of 2.80 g (16.2 mmol at 85%) of *m*-chloroperbenzoic acid in 50 mL of $CH_2Cl_2$ was added dropwise to a solution of 13.8 mmol of sulfide (either **7c**, **9a**, or **9c**) in 35 mL of $CH_2Cl_2$ at 0 °C. The mixture was allowed to stir at 0 °C overnight. Then it was diluted with 50 mL of $CH_2Cl_2$ and extracted with saturated aqueous $NaHCO_3$ solution (2 × 20 mL). The organic layer was dried over anhydrous $MgSO_4$, and the spent drying agent removed by filtration. The solvent was evaporated from the filtrate and replaced with 100 mL of toluene. This new solution was then heated at reflux for 2 h and cooled, and the solvent was removed by evaporation under vacuum.

From **7c**: 4.10 g of a yellow oil; NMR ($CCl_4$) analysis showed that in addition to other aromatic material (perhaps PhSSPh) this was a 60:40 mixture of **1a**/**2a**. No further isolation was attempted.

From **9a**: 3.73 g of a yellow oil; chromatography ($CHCl_3$) returned 2.90 g (83% yield) of an oil identical in all respects with **2a**.

From **9c**: 3.97 g of a yellow oil; chromatography ($CHCl_3$) returned 3.41 g (98% yield) of an oil identical in all respects with **1a**.

**Dimethyl 2-(Phenylsulfinyl)maleate (1b) and Dimethyl 2-(Phenylsulfinyl)fumarate (2b).** In each reaction 2.42 g (14.0 mmol at 85%) of *m*-chloroperbenzoic acid in 30 mL of $CH_2Cl_2$ was added dropwise to a solution of 3.02 g (12.0 mmol) of sulfide (either **1a** or **2a**) in 18 mL of $CH_2Cl_2$ at 0 °C. The solution was allowed to stir at 0 °C overnight. Then it was diluted with 40 mL of $CH_2Cl_2$ and extracted with saturated aqueous $NaHCO_3$ solution (2 × 20 mL). The organic layer was dried over anhydrous $MgSO_4$ and the spent drying agent removed by filtration. Evaporation of the solvent from the filtrate left a yellow oil in each case (3.34 g from **1a** and 3.19 g from **2a**). Column chromatography ($CHCl_3$) followed by Kugelrohr distillation (at 220 °C, 1.1 mm) yielded the purified materials.

**1b**: yellow oil; 2.61 g (82% yield); NMR ($CCl_4$) $\delta$ 7.55 (m, 5 H), 6.88 (s, 1 H), 3.58 and 3.76 (2 s, 6 H); IR (neat) 1723, 1645 $cm^{-1}$. Anal. Calcd for $C_{12}H_{12}O_5S$: C, 53.72; H, 4.51. Found: C, 53.59; H, 4.78.

**2b**: yellow oil; 2.57 g (81% yield): NMR ($CCl_4$) $\delta$ 7.50 (m, 5 H), 7.11 (s, 1 H), 3.66 and 3.81 (2 s, 6 H); IR (neat) 1723, 1635 $cm^{-1}$. Anal. Calcd for $C_{12}H_{12}O_5S$: C, 53.72; H, 4.51. Found: C, 53.88; H, 4.52.

**Dimethyl Bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (15).** Compound **1b** (2.00 g, 7.50 mmol) was adsorbed onto 10 g of silica gel[14] by dissolving the sulfoxide in $CH_2Cl_2$, adding the silica gel to this solution, and evaporating the $CH_2Cl_2$ on a rotary evaporator until dry powder was obtained. Then 12 mL of freshly distilled cyclopentadiene was added, the flask stoppered, and the mixture allowed to stir at room temperature for 24 h.

At the end of this time the mixture was filtered and the silica gel washed with successive portions of $CH_2Cl_2$ (about 100 mL total). Evaporation of the combined washings was followed by Kugelrohr distillation under high vacuum. The cyclopentadiene dimer easily distilled first followed by 1.24 g (80% yield) of the product (distilled at 170 °C and 1.3 mm). This product was identical in every way with dimethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate prepared separately from cyclopentadiene and dimethyl acetylenedicarboxylate.[15]

(14) Use of silica gel in Diels–Alder reactions was adapted from: Bartlett, P. D.; Blakeney, A. J.; Kimura, M.; Watson, W. H. *J. Am. Chem. Soc.* **1980**, *102*, 1383.

**2-(Phenylthio)bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic Anhydride (16a).** A solution of 2.00 g (9.71 mmol) of **13** and 2.0 mL of freshly distilled cyclopentadiene in 10 mL of ethyl ether was stirred at room temperature for 30 h. During this time the initially yellow solution became colorless. Evaporation of the solvent left 2.95 g of solid which, upon recrystallization from $CCl_4$–pentane, gave 2.19 g (83% yield) of white crystals: mp 90–92 °C; NMR ($CDCl_3$) $\delta$ 7.35–7.85 (m, 5 H), 6.37 (m, 2 H), 3.12–3.70 (m, 3 H), 2.35 (d, 1 H, $J$ = 9 Hz), 1.94 (d, 1 H, $J$ = 9 Hz); IR (KBr) 1862, 1780 $cm^{-1}$. Anal. Calcd for $C_{15}H_{12}O_3S$: C, 66.16; H, 4.44. Found: C, 66.44; H, 4.50.

**Registry No.** **1a**, 59790-39-5; **1b**, 84649-35-4; **2a**, 59790-38-4; **2b**, 84649-36-5; **3**, 624-48-6; **6a**, 785-44-4; **6b**, 84649-34-3; **7a**, 84649-29-6; **7c**, 84649-33-2; **8**, 25007-54-9; **9a**, 53256-00-1; **9c**, 84649-30-9; **10**, 108-31-6; **11**, 57242-92-9; **12**, 84649-31-0; **13**, 84649-32-1; **15**, 947-57-9; **16a**, 84649-37-6; PhSCl, 931-59-9; PhSH, 108-98-5; cyclopentadiene, 542-92-7.

(15) Diels, O.; Alder, K. *Justus Liebigs Ann. Chem.* **1931**, *490*, 236.

## 5-*tert*-Butyladamantan-2-one

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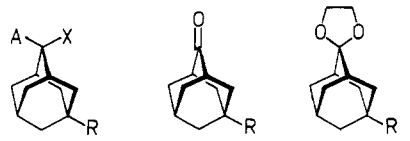
Studies of the stereochemistry of reactions at saturated carbon can basically be founded on the use of either chiral or geometrically isomeric substrates and products. The employment of enantiomers involves often knotty questions about their availability, optical purities, and relative configurations, but it has the advantage that only one isomer needs to be deployed since stereorandomness is defined, a priori, by the formation of a racemic product. The alternative[1] use of geometric isomers such as *E* and *Z* 4-substituted *tert*-butylcyclohexanes avoids the difficulties often associated with the use of chiral substrates but introduces another complication in that stereorandomness cannot then be equated with a 50:50 mixture of products, and hence both isomers must be studied.

1,4-Substituted adamantanes 1 offer a possible combi-




1 2 3

a, R = OH; b, R = COOMe; c, R = $CMe_2OH$; d, R = $CMe{=}CH_2$; e, R = $CMe(CH_2)_2$; f, R = $CMe_3$

nation of these advantages.[2] As both substituents A and X are simultaneously axial to one ring and equatorial to the other, there is no built-in thermodynamic prejudice toward one isomer on that account. One might seek to further reduce the possibility of a residual deviation from equal product free energies by a proper choice of the bridgehead substituent (e.g., with R = D). Two applica-

(1) See, for example: Kim, C. J.; Brown, H. C. *J. Am. Chem. Soc.* **1969**, *91*, 4286, 4287.

(2) The rigid and geometrically well-defined adamantane skeleton can obviously be used in a variety of stereochemical approaches; a brief survey of these may be found in: Nordlander, J. E.; Haky, J. E. *J. Org. Chem.* **1980**, *45*, 4782.

(3) Bone, J. A.; Pritt, J. R.; Whiting, M. C. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2644. Cloke, C.; Pritt, J. R.; Whiting, M. C. *Ibid.* **1972**, 2648.

0022-3263/83/1948-1099$01.50/0 

tions of such compounds have already been reported; one involved the solvolysis of tertiary substrates (A = R = Me),[3] and the other concerned the proposition of internal return in carbene formation (A = C≡CH, R = Ph).[4]

In each case, both isomers were available for use. In our supposition that a thermodynamic mixture of isomers should be close to 50:50 whatever the nature of R, we based ourselves upon the successful use of locking substituents in the 4-position of cyclohexanes. This device, introduced by Winstein in 1955, has permitted the measurements of *A* values[5] of substituents as a criterion of their size and stimulated the development of conformational analysis. Implicit in the use of such locks is the assumption that the large, equatorial 4-substituent employed exerts no effect on the site across the ring other than to freeze out ring reversal; direct steric or electronic influences are presumed to be negligible. We were therefore surprised to observe that the phenyl substituent in 1 clearly does have substantial directive effects in the ethynylation of 5-phenyladamantan-2-one and in both the neutral and base-promoted solvolyses of the corresponding chlorides (note that the substitution pattern is the same though the presence of the double bound oxygen forces a change in the numbering).[6] Others have likewise reported[7] encountering product ratios other than 1:1 in 1,4-substituted adamantanes. Our data were recently quoted by Cieplak in support of his new theory explaining the direction of nucleophilic attack upon carbonyl groups.[8]

5-Substituted adamantanones **2** thus clearly seem destined to play a role in several basic topics in organic chemistry, and we have begun a major study of them. As the first item on our agenda, we needed the *tert*-butyl-substituted ketone **2f**. Since a fair amount of effort was required to develop a multigram synthesis of this compound and since others may have an interest in it, we record our preparative route here.

## Discussion

The sequence of reactions is based on Geluk's discovery of a large-scale 5-hydroxylation of adamantanone[9] and on the successful Schleyer–Grob synthesis of 1-*tert*-butyladamantane.[10] Thus, the route essentially proceeds from the alcohol via Koch–Haaf carbonylation and methanol quenching to the carbomethoxy derivative and then via lithium methylation to the 2-propanol, dehydration to and cyclopropanation of the olefin, and finally reductive ring opening at the unencumbered cyclopropane bond as detailed in the Experimental Section. After the carbonylation, the ketone function was protected as the ethylene glycol ketal.

A few of the steps deserve comment. The carbonylation as reported by Lantvoev[11] requires 60% oleum; however, this reagent has become prohibitively expensive. We learned, fortunately, that 30% oleum works at least as well if only moderately elevated temperatures are used. For the cyclopropanation, we tried Helquist's new iron methylene-transfer reagent[12] and Kropp's photochemical methylene iodide treatment;[13] in neither method could we overcome the difficulties associated with incomplete conversion. Success was obtained with the repeated application of Suda's method,[14] which depends on diazomethane and a palladium acetate catalyst and which is said to be especially suitable for mono- or 1,1-disubstituted olefins. Results in the platinum-catalyzed ring opening depended critically on the use of a mixed solvent consisting of acetic acid and acetic anhydride: omission of the latter component led to premature removal of the protecting group and partial reduction of the ketone. While the alcohols could be reoxidized with pyridinium chlorochromate,[15] use of the mixed solvent obviated the problem.

## Experimental Section

**General Methods.** Melting and boiling points are uncorrected. $^1$H NMR spectra were recorded with either EM-360 or HFT-80 Varian instruments, $^{13}$C NMR spectra with a CFT-20, infrared spectra with a Perkin-Elmer Model 137 spectrometer, and mass spectra by means of a Hewlett-Packard 5980-A spectrometer. GC analyses were carried out with a Varian Aerograph Model 920 gas chromatograph with a 6-ft SE-30 column. Elemental analyses were done by Galbraith Laboratories, Inc.

**Materials.** 5-Hydroxyadamantan-2-one (**2a**; 12.3 g) was obtained in 78% yield by the oxidation of adamantanone (14.3 g) with anhydrous nitric acid[16] by means of Geluk's procedure.[9] Carbonylation was achieved by adding a solution of this sample in 75 mL of 97% formic acid (dried further by partial freezing) to 300 mL of 30% oleum at 60 °C over a 3-h period. An additional 75 mL of formic acid was then added in the next 2 h. After one additional hour, the mixture was poured slowly into 500 mL of methanol at 0 °C with magnetic stirring. After 2.5 h at room temperature, the resulting solution was concentrated by flash evaporation, the residue poured on 150 g of ice, and the solution extracted three times with 500 mL of methylene chloride; the extracts were combined and concentrated to 300 mL. After several washings with 100 mL of aqueous sodium chloride, the organic layer was dried over anhydrous sodium sulfate and concentrated to a pale yellow liquid which solidified upon cooling. Recrystallization in hexane gave 5-carbomethoxyadamantan-2-one (**2b**): 13.1 g (85%); mp 50–51 °C (lit.[11] mp 51–52 °C); $^1$H NMR ($CDCl_3$) $\delta$ 1.8–2.2 (m, 11 H), 2.5 (br s, 2 H), 3.5 (s, 3 H).

The entire sample of keto ester **2b** was converted into its ethylene ketal by dissolution in 250 mL of benzene, addition of 0.20 g of *p*-toluenesulfonic acid and 6 mL of ethylene glycol, and refluxing with a Dean–Stark trap dehydration apparatus for 7 h. After cooling, the benzene solution was washed with 100 mL of 10% aqueous sodium chloride solution and dried with potassium carbonate. The solvent was removed by flash evaporation, and the product was distilled at 1.5 mm in a 160 °C oil bath to give ketal **3b**: 14.7 g (93%); IR (neat) 2950 (s), 1740 (s), 1455 (m), 1230 (s), 1120 (s), 1100 (s), 930 (m) cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 1.5–2.2 (m, 13 H), 3.9 (s, 4 H), 3.6 (s, 3 H); $^{13}$C NMR ($CDCl_3$, $^1$H decoupled $\delta$ 177.6, 110.4, 64.4, 64.3, 51.7, 39.9, 38.5, 36.5 (2 C), 36.2 (2 C), 33.9 (2 C), 26.7. Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99. Found: C, 66.85; H, 7.84.

Product **3b** was converted in its entirety into 5-(2-hydroxy-2-propyl)adamantan-2-one ethylene ketal (**3c**) by dissolution in 300 mL of anhydrous ether and addition of 120 mL of 1.5 M methyllithium in ether (3 equiv) with vigorous stirring under a nitrogen atmosphere over 1.5 h. The reaction mixture was left at room temperature for 2–3 h, quenched with saturated am-

(4) le Noble, W. J.; Chiou, D. M.; Okaya, Y. *J. Am. Chem. Soc.* **1979**, *101*, 3244.
(5) Winstein, S.; Holness, N. J. *J. Am. Chem. Soc.* **1955**, *77*, 5562. Criticisms of this approach have appeared in the literature from time to time; thus, Kwart has reported finding apparently temperature-dependent *A* values (Mateos, J. L.; Perez, C.; Kwart, H. *J. Chem. Soc., Chem. Commun.* **1967**, 125) and Chadwick that the *tert*-butyl group causes considerable ring distortion Abraham, R. J.; Bergen, H. A.; Chadwick, D. J. *Tetrahedron Lett.* **1981**, *22*, 2807).
(6) le Noble, W. J.; Chiou, D. M.; Okaya, Y. *Tetrahedron Lett.* **1978**, 1961.
(7) See ref 3, footnote 22, for further examples.
(8) Cieplak, A. S. *J. Am. Chem. Soc.* **1981**, *103*, 4540.
(9) Geluk, H. W. *Synthesis* **1972**, 374.
(10) (a) Woodworth, C. W.; Buss, V.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1968**, 569. (b) Fischer, W. Grob, C. A.; Katayama, H. *Helv. Chim. Acta* **1976**, *59*, 1953.
(11) Lantvoev, V. I. *Russ. J. Org. Chem. (Engl. Transl.)* **1976**, *12*, 2292.
(12) Brandt, S.; Helquist, P. *J. Am. Chem. Soc.* **1979**, *101*, 6473.
(13) Kropp, P. J.; Pienta, N. J.; Sawyer, J. A.; Polniaszek, R. P. *Tetrahedron* **1981**, *37*, 3229.
(14) Suda, M. *Synth. Commun.* **1981**, 714.
(15) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647.
(16) Liang, P. "Organic Syntheses"; Wiley: New York, 1955; Collect. Vol. III, p 804.

monium chloride (10 mL), washed three times with aqueous sodium chloride, and dried over anhydrous sodium sulfate. Evaporation left a crude product which was purified by distillation at 1.5 mm with a 170 °C bath to give pure **3c**: 14.6 g (99%); IR (neat) 3540 (s), 2950 (s), 1125 (s), 1090 (m), 1070 (m), 925 (m) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.1 (s, 6 H), 1.5 (s, 1 H), 1.6–2.2 (m, 13 H), 3.9 (s, 4 H); $^{13}C$ NMR ($CDCl_3$, $^1H$ decoupled) $\delta$ 111.2, 64.3 (2 C), 36.7, 36.5 (2 C), 35.8, 35.4, 34.3 (2 C), 33.9 (2 C), 27.3, 24.6 (2 C). Anal. Calcd for $C_{15}H_{24}O_3$: C, 71.39; H, 9.59. Found: C, 71.58; H, 9.69.

Dehydration of this product to 5-isopropenyladamantan-2-one ethylene ketal (**3d**) was accomplished by heating with 20 g of potassium hydrogen sulfate (2–3 equiv) under nitrogen in a 170 °C bath for 4 h. A brown solid resulted which was extracted three times with 100-mL of chloroform. After evaporation, IR showed the product to be a mixture of ketone and ketal (peak at 1720 $cm^{-1}$); reketalization with 200 mL of benzene, 6 mL of ethylene glycol, and 0.01 g of *p*-toluenesulfonic acid in a Dean–Stark apparatus for 5 h as above gave after the workup and distillation at 1.5 mm and 130 °C pure 3d: 13.1 g (96.8%); IR (neat) 2930 (s), 1650 (m), 1440 (m), 1375 (m), 1180 (m), 1120 (s), 1070 (m), 955 (m), 920 (m), 890 (m) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.7 (t, $J$ = 1 Hz, 3 H), 1.4–2.1 (m, 13 H), 3.9 (s, 4 H), 4.7 (q, $J$ = 1 Hz, 2 H); $^{13}C$ NMR ($CDCl_3$, $^1H$ decoupled) $\delta$ 153.4, 111.2, 108.1, 64.3 (2 C), 40.6, 38.4 (2 C), 36.7 (3 C), 34.3 (2 C), 27.4, 18.8. Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 76.74; H, 9.43.

Cyclopropanation of this material was done in 3.0-g batches to give 5-(1-methylcyclopropyl)adamantan-2-one ethylene ketal (**3e**) as follows. A 50-mL ethereal solution of diazomethane[17] prepared from 5 g of *N*-methyl-*N*-nitrosoethylurea was added to 3.0 g (12.8 mmol) of the olefin in a 125-mL erlenmeyer flask with vigorous stirring at 0 °C. Palladium acetate (10 mg) was added in small portions over a period of 15 min. When gas evolution ceased, the mixture was filtered through a sintered-glass funnel, and the solvent was evaporated by flash evaporation; GC analysis showed that 30% conversion had occurred. The procedure was repeated four or five times until no further olefin was observable by GC. Fractional vacuum distillation of the residue yielded **3** as a colorless liquid: 2.41 g (9.7 mmol, 76%); bp 155 °C (1.5 mm); IR neat, 3010 (m), 2980 (s), 1440 (m), 1375 (m), 1125 (s), 1100 (m), 1070 (m), 1010 (m), 930 (m) $cm^{-1}$; mass spectrum, $m/e$ 248.2; $^1H$ NMR ($CHCl_3$) $\delta$ 0.0 (t, $J$ = 4 Hz, 2 H), 0.5 (t, $J$ = 4 Hz, 2 H), 0.9 (s, 3 H), 1.3–2.1 (m, 13 H), 3.9 (s, 4 H); $^{13}C$ NMR ($CDCl_3$, $^1H$ decoupled) $\delta$ 111.4, 64.3 (2 C), 38.6, 36.7 (2 C), 36.4 (2 C), 34.5 (2 C), 32.2, 27.5, 22.3, 21.2, 8.9 (2 C). Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.38; H, 9.74. Found: C, 77.23; H, 9.55.

Catalytic reduction of this cyclopropane derivative (2.4 g, 9.7 mmol) gave 5-*tert*-butyladamantan-2-one ethylene ketal (**3f**) as follows. A mixture with 500 mg of platinum(IV) oxide, 20 mL of glacial acetic acid, and 5 mL of acetic anhydride was subjected in a Parr apparatus to hydrogen at 60 °C and 60 psi for 36 h. The reaction mixture was filtered through a sintered-glass funnel, most of the solvent was removed by flash evaporation, 20 mL of water was added, and the mixture was extracted three times with 50 mL of methylene chloride. The organic extracts were combined, washed once with 10% sodium carbonate and three times with 100 mL of saturated sodium chloride solution, and dried over anhydrous sodium sulfate. The yellowish liquid obtained after evaporation of the solvent yielded 2.16 g (89%) of colorless liquid **3f** upon distillation at 165 °C (1.5 mm): $^1H$ NMR ($CDCl_3$) $\delta$ 0.9 (s, 4 H), 1.5–2.1 (m, 13 H), 3.9 (s, 4 H). This batch was not analyzed but was deprotected to 5-*tert*-butyladamantan-2-one **2f** by dissolution in 30 mL of methanol and 5 mL aqueous 1 M HCl and refluxing for 12 h. The resulting mixture was extracted three times with 100 mL of methylene chloride. The combined extracts were concentrated to 50 mL, washed once with 50 mL of 10% sodium carbonate and three times with 50 mL saturated sodium chloride solution, dried with anhydrous sodium sulfate, and flash evaporated to give a colorless liquid. Two successive sublimations at 90 °C (1.5 mm) gave white crystalline **2f**: 1.745 g (87%); mp 57–58 °C; IR ($CHCl_3$) 2980 (vs), 1720 (vs), 1475 (s), 1360 (s), 1280 (m), 1060 (s) $cm^{-1}$; mass spectrum, $m/e$ 206; $^1H$ NMR ($CDCl_3$) $\delta$ 0.85 (s, 9 H), 1.5–2.2 (m, 11 H), 2.5 (br s, 2 H); $^{13}C$ NMR ($CDCl_3$), $^1H$ decoupled) $\delta$ 219.4, 46.6 (2 C), 38.9 (2 C) 38.6 (2 C), 36.6, 35.4, 34.4, 28.2, 26.0 (3 C). Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.56; H, 10.71.

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**Registry No.** **2a**, 20098-14-0; **2b**, 56674-88-5; **3b**, 84454-62-6; **3c**, 84454-63-7; **3d**, 84454-64-8; **3e**, 84454-65-9; **3f**, 84454-66-0; **2f**, 84454-67-1; adamantanone, 700-58-3.

(17) Arndt, F. "Organic Syntheses"; Wiley: New York, 1943; Collect. Vol. II, p 165.

## 1-*tert*-Butyl-2-adamantanone

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As part of an investigation of steric effects on the interaction of ketones with lanthanide shift reagents, we needed to synthesize a sample of 1-*tert*-butyl-2-adamantanone (**4a**). We investigated the sequence shown in Scheme I which was developed by Schleyer and coworkers[1] for the preparation of 1-methyl-2-adamantanone (**4b**). The success of this approach despite several potential pitfalls prompts us to report the details of the synthesis.

4-Protoadamantanone (**1**) was prepared by the method of Majerski and Hameršak,[2] but the reaction of **1** with *tert*-butylmagnesium bromide was unsuccessful.[3] Consequently, we turned to the lithium derivative for which reduction was expected to be less important.[4a] The reaction of **1** with *tert*-butyllithium afforded a material which appeared to be a mixture of the desired product (**2a**) together with unreacted **1**. The proton NMR spectrum of the crude product exhibited a peak corresponding to a *tert*-butyl group, but the $^{13}C$ NMR spectrum still showed a peak corresponding to the carbonyl carbon of **1**. This suggested that a substantial fraction of the protoadamantanone had not undergone the desired *addition* reaction with *tert*-butyllithium but had instead been converted to the lithium enolate in an acid–base reaction. Such enolization is also well-precedented in the reactions of organometallic reagents with hindered ketones.[4,5] Since some of the desired addition had occured, the crude product was again subjected to treatment with *tert*-butyllithium, and the process was repeated several more times (for a total of five cycles) until no further decrease in the peak corresponding to the carbonyl group of **1** was observed in the $^{13}C$ NMR spectrum.

(1) Lenoir, D.; Glaser, R.; Mison, P.; Schleyer, P. v. R. *J. Org. Chem.* **1971**, *36*, 1821.
(2) Majerski, Z.; Hameršak, Z. *Org. Synth.* **1980**, *59*, 147.
(3) A small quantity of 1-adamantanol (**3c**) was obtained from this attempt, and this suggested that *reduction* to **2c** (followed by rearrangement, Scheme I) had occurred. Such reductions during attempts to prepare hindered tertiary alcohols via Grignard reactions are well precedented.[4]
(4) (a) Huet, F.; Emptoz, G. *J. Organomet. Chem.* **1975**, *101*, 139. (b) Whitmore, F. C.; George, R. S. *J. Am. Chem. Soc.* **1942**, *64*, 1239. (c) Cowan, D. O.; Mosher, H. S. *J. Org. Chem.* **1964**, *29*, 37.
(5) (a) Bartlett, P. D.; Tidwell, T. T. *J. Am. Chem. Soc.* **1968**, *90*, 4421. (b) Bohler, J. C. *J. Org. Chem.* **1973**, *38*, 904.

0022-3263/83/1948-1101$01.50/0 