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Friedel-Crafts Acylation of 2-Trimethylsilylnorbornene. Effect of Acyl Group on the Position of Attack

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Abstract: The acylation of 2-trimethylsilylnorbornene **1** in the presence of aluminium chloride gives minor quantities of the expected 2-norbornenyl ketones **4**. The formation of **3** and **5** as major products indicates that either α– or β–attack takes place predominantly depending on the nature of the acyl group, and the β-silicon effect is not a decisive factor. The β–silyl cation intermediate **2** mainly leads to nortricyclyl ketones **3** through 1,3-deprotonation, and the α-silyl cation **8** undergoes rearrangement to give novel bridge-head silylated products **5**.

Introduction

Vinylsilanes generally undergo facile regio- and stereo-specific displacement of silyl moiety by a variety of electrophiles due to the directive influence of silicon through stabilization of the intermediate β cation, called the β-silicon effect.[1] β-Silylated substrates experience maximum rate enhancement and furnish products of high stereoselectivity in their nucleophilic substitution[2] and β–elimination[1b-e,3] reactions if silicon and the leaving group can achieve a perfect antiperiplanar geometry in the transition state. The stereoelectronic effect of β-silicon in the antiperiplanar position has been shown to be operative even in the ground state of β-silyl esters.[4] The stereochemical outcome of electrophilic substitution reactions of the vinylsilanes is likewise governed by the β-silicon effect.[1b] The hyperconjugative overlap of C-Si σ bond with the empty *p* orbital on the β–carbenium ion formed by the addition of an electrophile can be achieved by a simple C_α-C_β bond rotation of 60° when severe restrictions are not encountered.[1e,5] In the case of the rigid 2-trimethylsilylnorbornene (**1**), the addition of an electrophile, e.g., R-C^+=O, generates the carbenium ion **2** (Scheme 1), that would enjoy only a partial stabilization by silicon as the C_2-Si σ bond and C_3-*p* empty orbital will be out of plane by a dihedral angle of about 30°.[6] However, if maximum overlap is achieved through the needed bond twist in **2** the Friedel-Crafts reaction of **1** would become an easy access to 2-norbornenyl ketones, e.g., **4a-d**, for which no simple preparative procedure exists,[7] though some of them find application in the synthesis of bicyclic alkaloids and terpenes.[8] The acylation of norbornene itself is seldom attempted, as the results do not seem to be useful.[9] The Friedel-Crafts acylation of even simple olefins is not an efficacious synthetic method because of the complexity

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of the products formed.[10] In contrast, the acylation of vinylsilanes is a smooth reaction that gives essentially pure products by both bimolecular as well as intramolecular processes, and has found wide application in the synthesis of a variety of α,β-unsaturated ketones of high purity and in excellent yields.[3b,5,11] We have studied the Friedel-Crafts acylation of **1** with aliphatic and aromatic acid chlorides. The products are found to vary according to the nature of the acyl group. The results are reported here.

Results and Discussion

2-Trimethylsilylnorbornene (**1**)[12a-c] was prepared from 2-chloronorbornene by Wurtz-Fittig type reaction that we had perfected for the preparation of cyclic vinylsilanes.[12d] The acylation of **1** was carried out using acetyl chloride, propionyl chloride, *n*-butyryl chloride, *iso*-butyryl chloride, benzoyl chloride and p-toluoyl chloride in the presence of aluminium chloride or stannic chloride as catalyst in methylene chloride as solvent at various temperatures. Stannic chloride was found to be unsuitable. With aluminium chloride the reactions occurred smoothly at about -20 °C.

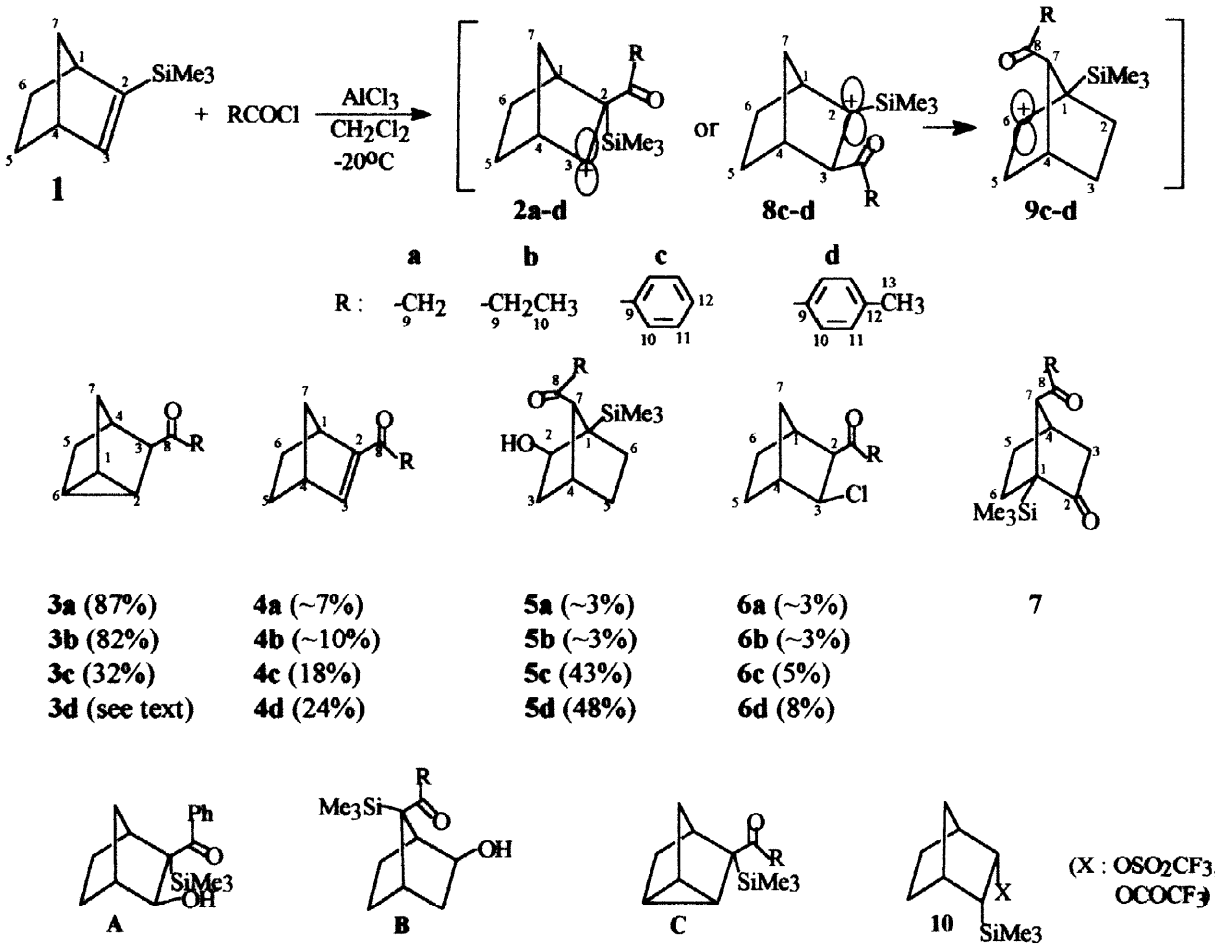
Acetylation. The reaction of **1** with acetyl chloride and aluminium chloride in methylene chloride at -25 °C gave a 95% yield of a product mixture, 87% of which was a single compound that was isolated in pure state by vacuum distillation followed by flash chromatography. It formed semicarbazone and 2,4-dinitrophenyl hydrazone derivatives. Its spectral and elemental analysis data and those of its derivatives established it as nortricyclyl methyl ketone **3a** that is reported in the literature.[13] A minor component (~7% of the mixture), very close to the major peak in GC, could not be obtained in sufficient purity for its unequivocal identification. However, its mass spectral pattern (GC-MS) suggested that it could be norbornenyl methyl ketone (**4a**) by comparison with that reported in the literature[7] and analogy with **4c** (see benzoylation). Two other minor products (~3% each) seem to be **5a** and **6a** from their GC-MS data. The acetylation reaction was repeated at various temperatures from -70 to +50 °C. The results of experiments conducted from -70 to -20 °C were identical, but became increasingly complex as the temperature was increased.

Propionylation. The results of propionylation of **1** with propionyl chloride were essentially similar to those of acetylation reaction. The product (yield, 92%) was found to consist of 82% of a compound that was isolated and identified as nortricyclyl ethyl ketone (**3b**) on the basis of its spectral characteristics. It formed semicarbazone. The product mixture also contained ~10% of another component (overlapping with **3b** in GC), which is likely to be norbornenyl ethyl ketone (**4b**). Two more minor products (3-4% each) are presumed to be **5b** and **6b** by comparing their GC-MS data with those of the analogous products in other acylation reactions.

Acylation with *n*-butyryl and *iso*-butyryl chlorides yielded considerably more complex mixtures of products, and the efforts expended to isolate the individual components in pure form by flash chromatography were futile. However, the GC-MS data indicated that some of them are analogous to those (**3-6**) observed in other acylation reactions of **1**. It was also possible to infer from the GC and NMR data of the partially purified products that the

relevant norbornenyl ketones could constitute about 15-20% of the mixture, particularly in the case of *iso*-butyryl chloride.

Scheme 1



Benzoylation. The reaction of **1** with benzoyl chloride in the presence of aluminium chloride in methylene chloride at -20 °C gave 90% yield of a mixture of three major products, which were isolated by flash chromatography. In order of their elution, the first, second and third components constituted 32%, 18% and 43% of the mixture, and were identified as nortricyclyl phenyl ketone (**3c**), norbornenyl phenyl ketone (**4c**) and 1-trimethylsilyl-2-hydroxybicyclo[2.2.1]hept-7-yl phenyl ketone (**5c**), respectively. The ketone **3c**, an intermediate used in the synthesis of some spasmolitic, antiallergic and antidepressant drugs,[14] and the ketone **4c**[15] are described in the literature, and their structural characterization was accomplished by comparison of their physical and spectral properties with those reported. The structural identification of the third component posed some problem. Its IR, ^{1}H NMR, ^{13}C NMR, MS and elemental analysis data indicated that it could be represented as **A** or **B** or **5c**. However, an important clue for suggesting its structure as **5c** stemmed from the fact that the trimethylsilyl group was still securely present in it. If it had the structure **A** or **B**, the trimethylsilyl group would not have survived through the process of reaction and work up, as α-silyl ketones are known to undergo loss of

silicon fairly readily under acidic conditions by desilylative enolization.[16] In fact, the silicon-free nortricyclyl ketones **3a-c** could well have formed from their silylated precursors C (Scheme 1). It may also be noted in this connection that the acylation of 1-trimethylsilylcyclooctene was earlier observed to give only silicon-free bicyclo[3.3.0]octyl alkyl/aryl ketones.[17] Among the three structures (**A**, **B** and **5c**) under consideration, only **5c** cannot enolize, as the silyl group is on the bridge-head and β to the keto function. Further, on oxidation with Jones reagent, the compound produced a diketone which still retained the silyl group. Such a tight attachment of silicon clearly indicated that silicon was on the bridge-head carbon, and the diketone should have the sructure **7** and hence its precursor should be **5c**. Finally, the structure **5c** was conclusively solved by its single crystal X-ray analysis. The ORTEP structure of **5c** is given in figure 1. A minor component (4-5%) of the benzoylation reaction mixture, eluted before **3c**, is likely to be the chloroketone **6c** based on its NMR and MS data.

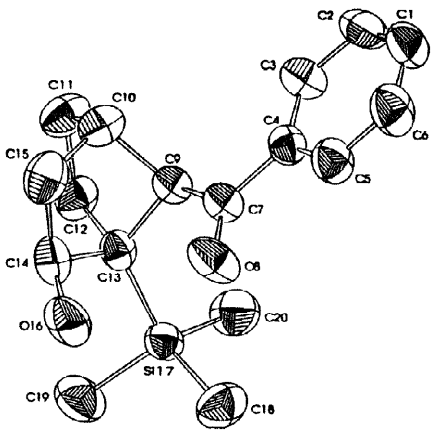


Figure 1. The ORTEP diagram of **5c**

p-Toluolyation. The aluminium chloride catalysed reaction of **1** with p-toluoyl chloride gave a rather more complex mixture of products than the one obtained in the case of benzoylation. However, we could isolate, in order of their elution, **6d**, **4d** and **5d** which were in about 8%, 24% and 48% proportion respectively, in the reaction mixture. The spectral data of **4d**, **5d** and **6d** compared very nicely with those of **4c**, **5c** and **6c** with the essential difference arising from the presence of p-methyl group in the aromatic ring. Isolation and identification of **3d** could not be accomplished in spite of several attempts under various reaction conditions.

An important observation that should be addressed, first of all, while analysing the results is the question why the expected norbornenyl ketones **4a-d** are not the major products. This should have been the case if it is assumed, as with other vinylsilanes,[11] that the acyl group attacks **1** at the silylated carbon (C_2) to form the β-silyl cation **2**, which is normally expected to undergo the double-bond-forming desilylation, because the β-silylated carbocation is believed to lose the silyl group more rapidly than the β-hydrogen or is captured by a nucleophile.[5] The formation of the nortricyclyl ketones **3a** and **3b** as almost the sole products clearly shows that the loss of proton on C_5 (in **2a** and **2b**) takes place more readily than the loss of β-silicon during acetylation and propionylation. This implies that the C_5-H σ bond is better positioned for a more effective overlap with the C_3-*p*

empty orbital than the C_2-Si σ bond is oriented for the required magnitude of hyperconjugation, that is, the C_3-*p* orbital and C_2-Si σ bond are out of the needed coplanarity (by ~30°). Though the parent norbornene usually yields nortricyclyl derivatives and Wagner-Meerwein rearrangement products in many of its electrophilic reactions,[18] it has been reported, however, to give no such products on Friedel-Crafts acetylation.[9]

Lambert and Chelius have shown that participation of the silyl group occurs to a significant extent in the solvosis of **10** in which C_2-Si and C_3-X bonds are coplanar. However, they concluded that the β-silicon effect was far less here than what they observed it for an antiperiplanar interaction.[19] Though the acetylation of **1** is expected to give β-cation intermediate of a similar type, the transition state geometries in the two cases are likely to differ considerably,[19] and the C_2-Si σ C_3-*p* interaction in **2** during acylation may not be effective enough for the expected desilylative double bond formation.[20] An alternative possiblity is that, if the C_5-H loss is faster than the silicon elimination, then nortricyclane derivative (**3**) would form preferentially. The third possiblity is the formation of norbornenyl ketones **4a-c** as primary products which then transform into nortricyclyl ketones **3a-c**. To ascertain this possiblity, **4c** was treated with aluminium chloride under identical conditions used for the benzoylation of **1**. However, **3c** was not detected indicating that **4c** was not its precursor. On this ground, we presume that **3a** and **3b** are also formed directly from **2a** and **2b** and not *via* **4a** and **4b**, respectively.

The formation of **5c** and **5d** as major products of benzoylation and p-toluoylation of **1** is an interesting result. The presence of the hydroxy group in these molecules can be rationalized by assuming that the precursor cation intermediates **9c** and **9d** survive until the addition of water during work up. The cations **9c** and **9d** can be visualized to have formed via Wagner-Meerwein rearrangement of the α-silyl cations **8c** and **8d** generated by the attack of acylium ion on the β carbon competing with the α attack that would lead to the more stable β-cation. Taking into account the fact that acetylation and propionylation of **1** do not give similar products **5a** and **5b** in any significant quantity, we think that the formation of **8c** and **8d** is a result of steric effect. Since the benzoyl and p-toluoyl groups are much bulkier than the acetyl or propionyl group, the former are certain to encounter greater resistance from the silyl moiety for α-attack. This means that in the benzoylation and p-toluoylation cases there is a fine balancing between the greater stability of the secondary β-silyl cation (**2c** and **2d**) versus the tertiary α-silyl cation (**8c** and **8d**) and the steric hindrance to α-attack, as the energy difference between the α- and β-cations (**8** and **2**) may not be sufficiently large to overcome the steric crowding in the transition state following the α-attack.[1a,1g,19,21] It may also be borne in mind that norbornyl cations (classical or nonclassical) have addditional stabilizing features,[18] which should be true of **2**, **8** and **9** as well. However, the α-silyl cations **8c** and **8d** appear to be the least stable, as no unrearranged products which can be considered to be directly originating from them are observed. An important factor that gives long life (i.e., until work up) to the cation **9c** or **9d** is probably the interaction of its empty *p* orbital with the aromatic ring or the oxygen lone pair on benzoyl C=O, which is located on the same side. Our attempt to characterize the cation **9c** in an NMR tube experiment was unsuccessful because of the formidable complexity of the observed ^1H and ^{13}C spectra.

The formation of the unsaturated ketones **4c** and **4d** in higher proportions than **4a** or **4b** is also noteworthy. We presume that these results are again a consequence of the size of the acylating group. Since a bigger acyl group could push the silyl moiety in **2** further towards the endo side, a more favourable alignment of the C_2-Si σ bond with the C_3-*p* orbital can occur during benzoylation or p-toluoylation. A similar trend is noted in the case of the reaction of 1 with *iso*butyryl chloride, where the expected unsaturated ketone seems to be >20% (from the ^{1}H NMR spectrum of the reaction mixture), though it could not be accurately measured.

Conclusion

The acylation of 1-trimethylsilylnorbornene (**1**) does not provide the expected α,β-unsaturated ketones exclusively, but other interesting products are formed, which vary depending on the nature of acyl chloride. The direction of attack of the acyl cation seems to depend upon both electronic and steric factors. The latter becomes prominent when the acyl group is large and this leads to the products of attack at the less hindered β position that first produces the less stable α-silyl cation **8c/8d** and then the rearranged cation **9c/9d**. The β-cation **2** is presumed to lead to the nortricyclyl ketones **3** in preference to the expected unsaturated ketones **4**. In any case, the intermediates **2**, **8**, and **9** of both α- and β-attack, being norbornyl cations, could benefit from their nonclassical/classical nature.

Experimental Section

Infrared spectra were recorded on Beckman 4260 instrument using thin films of liquid samples between KBr plates, and KBr pellets of solid samples. The ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC-250 instrument and the chemical shift values (δ) are reported relative to tetramethylsylane and $CDCl_3$ respectively. The ^{13}C NMR assignments are based on the off-resonance decoupled and DEPT spectra. The mass spectra were obtained on a Hewlett-Packard 5985B instument attached to HP 5840A gas chromatograph. Gas chromatographic (GC) analysis was carried out on HP 5890A instrument using 50 m SE 54 capillary column with a temperature programme of 50 to 180 °C at 7 °C/min. Flash chromatography was carried out under 2.5 atmospheric pressure of nitrogen on silica gel (Merck), the eluted solution being continuously monitored by a Knauer UV-visible spectrophotometer. Elemental analyses were performed at Engler-Bunte Institut Bereich I, Universitat Karlsruhe, Germany. Melting points were determined using open capillaries and were uncorrected.

Dichloromethane was distilled over P_2O_5 and ether was distilled over sodium wire for reactions. The solvents used for column chromatography were purified by simple distillation. For TLC analysis, pre-coated Kieselgel 60 F_{254} plates (Merck) were used. All reagents were commercial grade and their purity was checked before use.

2-Trimethylsilylbicyclo[2.2.1]hept-2-ene (**1**). A mixture of 6.21 g (0.27 mol) of finely cut sodium, 19.86 g (0.183 mol) of chlorotrimethylsilane and 11.91 g (0.095 mol) of 2-chloronorbornene[22] in 150 mL of ether was stirred and refluxed at a bath temperature of 60-70 °C, the condenser being fitted with a $CaCl_2$ drying tube. The reaction was followed by G.C., and at the end of ~80 h 2-chloronorbornene had disappeared. The mixture was cooled and filtered through a plug of glass wool. The solid was washed with 20 mL of ether. The combined ether

filtrates were carefully treated with water (120 mL). After separating the aqueous layer, the ether layer was washed successively with water (120 mL), sat $NaHCO_3$ solution (120 mL) and water. The solution was then dried over Na_2SO_4, the solvent was removed and the residue was distilled. Pure colourless 2-trimethylsilylnorbornene[12a-c] was collected at 81-83 °C/37 Torr (Lit[12c] b.p. 30 °C/0.6 Torr); yield, 11.5 g (74%).

***Acetylation of* 1.** To a suspension of 2.20 g (16.5 mmol) of anhydrous $AlCl_3$ in 35 mL of dry methylene chloride in a 100 mL three necked flask fitted with a condenser with a drying tube, a low temperature thermometer and a dropping funnel, stirred at -5 °C under nitrogen atmosphere, was added 1.25 g (16.0 mmol) of acetyl chloride. The mixture was stirred at room temperature for 5 min and then cooled to -25 °C. A solution of 1.672 g (10.1 mmol) of **1** in 5 mL of methylene chloride was added dropwise over a period of 20 min, the temperature being maintained at -25 °C. After stiring for an additional 10 min, the mixture was added to 50 g of ice-water. The organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (20 mL) and the combined organic layers were washed successively with sat $NaHCO_3$ solution (2 X 50 mL), water (50 mL) and sat NaCl solution (50 mL) and dried over Na_2SO_4. Concentration of the solution gave a colourless liquid, yield, 1.26 g (93%), the GC of which showed a major peak, constituting about 84% of the mixture, followed by ~7 smaller peaks. Among the minor components, three were inferred to be **4a**, **5a** and **6a** from their mass spectral patterns (GC-MS) and the others as their isomers (on comparison with similar products of benzoylation and p-toluoylation). The main product, tricyclo[2.2.1.$0^{2,6}$]hept-3-yl methyl ketone (**3a**),[13] a colourless liquid with a fragrant odour reminiscent of freshly cut fir leaves, was obtained in >99% purity by distillation (fraction boiling at 87-90 °C/14 Torr), followed by flash chromatography on silica gel using pentane as eluant. IR: 1705 cm^{-1}. ^1H NMR: δ 2.43 (s, C_3-*H*), 2.22 (narrow m, C_4-*H*), 2.15 (s, -CH_3), 1.38 (m, 2 H), 1.35-1.15 (two overlapping m, 5 H). ^{13}C NMR: δ 210.0 (s, C_8), 57.9 (d, C_3), 34.7 (t, C_7), 33.1 (d, C_4), 30.3 (t, C_5), 29.1 (q, C_9), 12.3 (d, C_2), 11.5 (d, C_1), 10.1 (d, C_6). DEPT spectrum confirms this assignment. MS: *m/z* (relative intensity) 136 (46, M^+), 121 (17), 93 (71), 91 (100), 78 (27), 77 (83), 66 (20), 65 (22), 58 (42), 43 (81), 39 (40). Anal. Found: C, 79.18; H, 8.74. $C_9H_{12}O$ calc.: C, 79.41; H, 8.82%. 2,4-Dinitrophenylhydrazone, m.p. 166 °C. Anal. Found: C, 56.68; H, 5.04; N, 17.45. $C_{15}H_{16}N_4O_4$ calc.: C, 56.96; H, 5.06; N, 17.72%. Semicarbazone, m.p. 194 °C. Anal. Found: C, 61.92; H, 7.95; N, 21.51. $C_{10}H_{15}N_3O$ calc.: C, 62.17; H, 7.77; N, 21.76%.

***Propionylation of* 1.** To 3.576 g (26.8 mmol) of $AlCl_3$ in 40 mL of CH_2Cl_2 at -5 °C was added 2.506 g (27.1 mmol) of propionyl chloride with stirring. The mixture was further cooled to -25 °C and 2.478 g (14.9 mmol) of **1** was added dropwise over a period of 20 min, the temperature being maintained at -25 °C. After stirring for 30 min more, the product was worked up as in the previous experiment; yield, 2.06 g (92%). The GC showed a major peak (82%) closely associated with a peak of ~10% area and a few minor peaks at higher retention times. The major component, tricyclo[2.2.1.$0^{2,6}$]hept-3-yl ethyl ketone (**3b**), a colourless liquid with odour similar to that of **3a**, was isolated by distillation (b.p. 64-67 °C/3 Torr) followed by flash chromatography as in the case of acetylation product. IR: 1710 cm^{-1}. ^1H NMR: δ 2.46 (q, *J*=7.3 Hz, -CO-CH_2-), 2.42 (s, C_3-*H*), 2.21 (narrow q,

J=0.7 Hz, C_4-*H*), 1.38 (m, 2H), 1.35-1.16 (m, 5H), 1.03 (t, *J*=7.3 Hz, 3H). ^{13}C NMR: δ 212.4 (s, C_8), 56.9 (d, C_3), 34.8 (t, C_7), 34.6 (t, C_9), 33.1 (d, C_4), 30.3 (t, C_5), 12.2 (d, C_2), 11.3 (d, C_1), 10.1 (d, C_6), 7.7 (q, C_{10}). DEPT spectrum confirms the assignments. MS: *m/z* (relative intensity) 150 (39, M^+), 121 (26), 93 (89), 91 (100), 79 (12), 78 (28), 77 (76), 72 (24), 66 (20), 65 (29), 57 (83), 51 (21), 41 (27), 39 (68), 29 (57), 27 (41). Anal. Found: C, 79.86; H, 9.42. $C_{10}H_{14}O$ calc.: C, 80.00; H, 9.33%. Semicarbazone, m.p. 206 °C. Anal. Found: C, 63.59; H, 8.16; N, 20.50. $C_{11}H_{17}N_3O$ calc.: C, 63.77; H, 8.21; N, 20.29%. 2,4-Dinitrophenylhydrazone, m.p. 123 °C. MS of minor (10% **4b**) component: *m/z* (relative intensity) 150 (13, M^+), 121 (27), 93 (100), 77 (10), 65 (46), 51 (10), 39 (36), 29 (20), 27 (19).

***Benzoylation of* 1.** To a suspension of 3.70 g (27.7 mmol) of anhydrous $AlCl_3$ in 50 mL of CH_2Cl_2 at -10 °C stirred under nitrogen atmosphere was added 3.84 g (27.4 mmol) of benzoyl chloride in 5 mL of CH_2Cl_2 dropwise. When the mixture became homogeneous, it was cooled to -25 °C, and a solution of 2.606 g (15.7 mmol) of **1** in 7 mL of CH_2Cl_2 was added over a period of 20 min. The GC taken immediately after the completion of the addition showed no presence of the starting compound (**1**). After stirring for another 30 min (the GC showed no significant change), the mixture was poured into ice-cold water (100 mL), the layers were separated and the aqueous layer was extracted with 25 mL of CH_2Cl_2. The combined organic layers were washed with 10% NaOH solution until free from benzoyl chloride and benzoic acid, then with sat $NaHCO_3$ (75 mL), water (2 X 75 mL), sat NaCl solution (75 mL), dried (Na_2SO_4) and concentrated. TLC on Kieselgel 60 F_{254} (Merck) with 3% ether in pentane as eluant showed four spots, R_f values: 0.80, 0.57, 0.47 and 0.15. Flash chromatography on silica gel column gave 0.17 g (eluant: 2.5% ether in pentane) of a compound likely to be 3-chlorobicyclo[2.2.1]hept-2-yl phenyl ketone (**6c**). IR: 1680 cm^{-1}. ^{1}H NMR: δ 7.97 (d, *J*=8.0 Hz, 2H), 7.57 (t, *J*=8.0 Hz, 1H), 7.47 (t, *J*=8.0 Hz, 2H), 4.59 (narrow t, *J*=2.5 Hz, 1H), 3.97 (narrow m, 1H), 2.73 (narrow m, 1H), 2.50 (d, *J*=4.9 Hz, 1H), 2.16 (d, *J*=10.0 Hz, 1H), 1.72-1.56 (tt, *J*=12.5, 4.5 Hz, 1H), 1.48 (d, *J*=10.0 Hz, 1H), 1.45-1.15 (m, 2H), 1.00 (narrow m, 1H). MS: *m/z* (relative intensity) 236 (3, M^+), 234 (9, M^+), 199 (15), 169 (9), 167 (26), 133 (27), 105 (100), 66 (30), 51 (52), 39 (28).

Elution with 3% ether in pentane gave 0.88 g of **3c** and 0.49 g of **4c**. Finally, elution with 25% ether in pentane gave 1.74 g of **5c**.

Tricyclo[2.2.1.0^{2,6}]hept-3-yl phenyl ketone (3c).[14] White crystalline solid, b.p. (Kugelrohr distillation) 100 °C/0.001 Torr, m.p. 57 °C (Lit[14] b.p. 110-121 °C/0.01 Torr, m.p. 56 °C). IR: 1680 cm^{-1}. ^{1}H NMR: δ 7.96 (d, *J*=7.0 Hz, 2H), 7.56 (t, *J*=7.0 Hz, 1H), 7.45 (t, *J*=7.0 Hz, 2H), 3.27 (s, 1H), 2.25 (broad s, 1H), 1.60 (d, *J*=10.3 Hz, 1H), 1.48-1.35 (m, 3H), 1.35-1.15 (m, 3H). ^{13}C NMR: δ 200.9 (s, C_8), 137.2 (s, C_9), 132.6 (d, C_{12}), 128.4 (d, C_{10}), 128.1 (d, C_{11}), 53.2 (d, C_3), 35.1 (t, C_7), 34.5 (d, C_4), 30.2 (t, C_5), 13.2 (d, C_2), 11.1 (d, C_1), 10.3 (d, C_6). DEPT spectrum confirms the assignments. MS: *m/z* (relative intensity) 198 (24, M^+), 120 (15), 105 (100), 91 (20), 77 (69), 51 (34), 39 (17). Anal. Found: C, 84.61; H, 7.30. $C_{14}H_{14}O$ calc.: C, 84.85; H, 7.07%.

Bicyclo[2.2.1]hept-2-en-2-yl phenyl ketone (4c).[15] White crystalline solid (recrystallized from aqueous ethanol), m.p. 79 °C (Lit[15] m.p. 77-78 °C). IR: 1620 cm^{-1}. ^1H NMR: δ 7.74 (d, *J*=7.0 Hz, 2H), 7.52 (t, *J*=7.0 Hz, 1H), 7.42 (t, *J*=7.0 Hz, 2H), 6.66 (d, *J*=3.0 Hz, 1H), 3.47 (broad s, 1H), 3.13 (broad s, 1H), 1.82 (m, 2H), 1.58 (dt, *J*=7.5, 2.0 Hz, 1H), 1.27 (dd, *J*=8.0, 1.0 Hz, 1H), 1.20 (tt, *J*=7.3, 2.0 Hz, 1H), 1.10 (tt, *J*=7.2, 2.0 Hz, 1H). ^{13}C NMR: δ 192.7 (s, C_8), 149.5 (d, C_3), 148.7 (s, C_2), 138.4 (s, C_9), 131.9 (d, C_{12}), 128.9 (d, C_{10}), 128.2 (d, C_{11}), 47.2 (t, C_7), 44.4 (d, C_1), 42.5 (d, C_4), 25.4 (t, C_6), 24.7 (t, C_5). DEPT spectrum confirms the assignments. MS: *m/z* (relative intensity) 198 (30, M^+), 170 (43), 105 (100), 93 (14), 77 (56), 65 (28), 51 (36), 39 (20). Anal. Found: C, 84.75; H, 7.17. $C_{14}H_{14}O$ calc.: C, 84.85; H, 7.07%.

1-Trimethylsilyl-*exo*-2-hydroxybicyclo[2.2.1]hept-*syn*-7-yl phenyl ketone (5c). White crystalline solid (recrystallized from aqueous ethanol), m.p. 116 °C. IR: 3400, 1665 cm^{-1}. ^1H NMR: δ 7.99 (d, *J*=6.5 Hz, 2H), 7.60 (t, *J*=6.5 Hz, 1H), 7.49 (t, *J*=6.5 Hz, 2H), 5.00 (d, *J*=12.1 Hz, -O*H*), 3.82 (septet, *J*=3.5 Hz, 1H), 3.40 (s, 1H), 2.65 (t, *J*=3.5 Hz, 1H), 1.94 (dd, *J*=13.5, 7.5 Hz, 1H), 1.82-1.53 (m, 3H), 1.25 (two overlapping quartets, 2H), 0.06 (s, 9H). ^{13}C NMR: δ 204.8 (s, C_8), 137.7 (s, C_9), 133.4 (d, C_{12}), 128.7 (d, C_{10}), 128.4 (d, C_{11}), 78.7 (d, C_2), 58.8 (d, C_7), 45.4 (d, C_4), 44.5 (s, C_1), 43.2 (t, C_3), 30.7 (t, C_6), 29.5 (t, C_5), -1.5 (q, $Si(CH_3)_3$). DEPT spectrum confirms the assignments. MS: *m/z* (relative intensity) 288 (10, M^+), 273 (16), 260 (16), 259 (17), 245 (22), 244 (66), 183 (19), 181 (10), 172 (32), 157 (17), 155 (19), 129 (24), 128 (17), 115 (14), 105 (83), 91 (17), 77 (82), 75 (63), 73 (100), 67 (27), 59 (13), 55 (11), 51 (26), 47 (21), 45 (68), 43 (27). Anal. Found: C, 70.82; H, 8.50. $C_{17}H_{24}O_2Si$ calc.: C, 70.83; H, 8.33%.

X-Ray Crystallographic Data: Single crystals of **5c** suitable for X-ray crystallographic study were obtained from chloroform solution by slow evaporation. The crystals were monoclinic, space group $P2_1/a$: a=13.517(3) A, b=6.579(2) A, and c=18.924(3) A, β=102.77(1). The calculated density is 1.167 g/cm^3 for z=4. The data were collected on a Rigaku AFC7S diffractometer with Mo Kα (λ=0.7107 A) radiation using the ω/2θ scan mode upto a θ limit of θ < 25°. Of the 3027 reflections collected, 2887 reflections were significant [I > 2σ (I)]. The structure was solved by direct methods using SHELX-86.[23] The refinement of positional and anisotropic thermal parameters with a full-matrix least squares method using SHELXL-93[24] converged to final R=0.044 and R_w=0.114. The final difference Fourier map was featureless with $\Delta\rho_{min}$= -0.286 e/A^3. The goodness-of-fit on F_o^2 is 0.525. The weighting scheme employed is given by the formula, $w=1/[\sigma^2(F_o^2) + (0.1116p)^2 + 4.787p]$, where $p=(F_o^2 + 2F_c^2)/3$.

***Oxidation of* 5c to 1-trimethylsilyl-2-oxobicyclo[2.2.1]hept-*syn*-7-yl phenyl ketone (7).** Chromium trioxide (1.81 g, 18.1 mmol) was dissolved in a solution of 2.66 g (36.67 mmol) of pyridine in 25 mL of dry CH_2Cl_2. To the resulting mixture was added 0.362 g (1.26 mmol) of **5c** and stirred for 2 h at room tempeature. Then, 25 mL of water was added, the precipitated solid was filtered off and the organic layer was separated, which was washed successively with water (2 X 25 mL), dil HCl (2 X 25 mL), sat $NaHCO_3$ solution (25 mL), sat NaCl solution (25 mL) and dried (Na_2SO_4). The solvent was removed and the solid product was purified by passing

through a silica gel column with 25% ether in pentane as eluant to obtain a white crystalline compound, yield, 0.33 g (92%), m.p. 145 °C. IR: 1720, 1665 cm^{-1}. ^1H NMR: δ 7.99 (d, *J*=7.2 Hz, 2H), 7.57 (t, *J*=7.2 Hz, 1H), 7.46 (t, *J*=7.2 Hz, 2H), 3.58 (t, *J*=1.8 Hz, 1H), 2.82 (narrow m, 1H), 2.24 (d with fine splitting, *J*=17.4, 2.3 Hz, 1H), 1.99 (narrow m, 2H), 1.70 (dd, *J*=17.5, 2.0 Hz, 1H), 1.52 (m, 2H), 0.07 (s, 9H). ^{13}C NMR: δ 216.8 (s, C_2), 199.9 (s, C_8), 136.8 (s, C_9), 133.4 (d, C_{12}), 128.9 (d, C_{10}), 128.1 (d, C_{11}), 59.8 (d, C_7), 50.0 (s, C_1), 42.7 (t, C_3), 42.0 (d, C_4), 29.6 (t, C_6), 28.2 (t, C_5), -2.4 (q, $Si(CH_3)_3$). DEPT spectrum confirms the assignments. MS: *m/z* (relative intensity) 286 (40, M^+), 271 (22), 245 (90), 243 (17), 217 (24), 105 (32), 77 (43), 75 (22), 73 (100), 45 (30). Anal. Found: C, 71.28; H, 7.64. $C_{17}H_{22}O_2Si$ calc.: C, 71.33; H, 7.69.

***p-Toluoylation of* 1.** The reaction of **1** (1.36 g, 8.2 mmol) with p-toluoyl chloride (1.87 g, 12.2 mmol) and aluminium chloride (1.70 g, 12.8 mmol) in 25 mL of CH_2Cl_2 under the same experimental conditions that were employed for benzoylation, gave a mixture (yield, 1.90 g, 95%) of products. TLC on silica gel (eluant, 1:1 pentane-ether) showed five spots (R_f values: 0.85, 0.59, 0.54, 0.46 and 0.24). On flash chromatography (eluant, 1:9 ether-pentane), three components (corresponding to the first, fourth and fifth spots on TLC) could be obtained in pure form and identified as **6d** (0.19 g, 8%), **4d** (0.57 g, 24%) and **5d** (1.12 g, 48%) respectively. Since the components corresponding to the second and third spots in TLC could not be separated from each other or from other minor impurities, they were left unidentified. However, we believe that one of them is probably **3d**.

Bicyclo[2.2.1]hept-2-en-2-yl p-toluyl ketone (4d). White solid, m.p. 88 °C. IR: 1625, 1590 cm^{-1}. ^1H NMR: δ 7.67 (d, *J*=6.4 Hz, 2H), 7.22 (d, *J*=8.4 Hz, 2H), 6.63 (d, *J*=3.2 Hz, 1H), 3.45 (s, 1H), 3.11 (s, 1H), 2.40 (s, 3H), 1.81 (m, 2H), 1.56 (d, *J*=8.9 Hz, 1H), 1.26 (d, *J*=8.7 Hz, 1H), 1.22 (t, *J*=8.8, 1H), 1.08 (t, *J*=8.8, 1H). ^{13}C NMR: δ 192.5 (C_8), 148.7 (C_9), 148.6 (C_3), 142.4 (C_2), 135.6 (C_{12}), 129.0 (C_{10}), 128.8 (C_{11}), 47.1 (C_7), 44.3 (C_1), 42.6 (C_4), 25.4 (C_6), 24.7 (C_5), 21.5 (C_{13}). MS: *m/z* (relative intensity) 212 (21, M^+), 184 (35), 169 (10), 156 (9), 119 (100), 91 (51), 77 (11), 65 (31). Anal. Found: C, 85.21; H, 7.47. $C_{15}H_{16}O$ calc.: C, 84.90; H, 7.55%.

1-Trimethylsilyl-*exo*-2-hydroxybicyclo[2.2.1]hept-*syn*-7-yl p-toluyl ketone (5d). White solid, m.p. 130 °C. IR: 3400, 1660 cm^{-1}. ^1H NMR: δ 7.89 (d, *J*=8.2 Hz, 2H), 7.28 (d, *J*=8.2 Hz), 5.07 (d, *J*=12.0 Hz, -O*H*), 3.81 (septet, *J*=3.5, 1H), 3.38 (s, 1H), 2.62 (t, *J*=3.5 Hz, 1H), 2.43 (s, 3H), 1.93 (dd, *J*=13.4,7.4 Hz, 1H), 1.80-1.57 (m, 3H), 1.26-1.08 (m, 2H), 0.05 (s, 9H). ^{13}C NMR: δ 104.3 (C_8), 144.3 (C_9), 135.1 (C_{12}), 129.4 (C_{10}), 128.6 (C_{11}), 78.7 (C_2), 58.6 (C_7), 45.4 (C_4), 44.3 (C_1), 43.2 (C_3), 30.7 (C_6), 29.5 (C_5), 21.6 (C_{13}), -1.51 (-$Si(CH_3)_3$). MS: *m/z* (relative intensity) 302 (2, M^+), 287 (4, M^+-15), 258 (12), 212 (6), 186 (18), 183 (14), 169 (20), 119 (93), 91 (77), 75 (59), 73 (100), 67 (16), 65 (15). Anal. Found: C, 71.74; H, 8.72. $C_{18}H_{26}O_2Si$ calc.: C, 71.52; H, 8.61%.

3-Chlorobicyclo[2.2.1]hept-2-yl p-toluyl ketone (6d). White solid, m.p. 105 °C. IR: 1680 cm^{-1}. ^1H NMR: δ 7.87 (d, *J*=8.2 Hz, 2H), 7.27 (d, *J*=8.2 Hz, 2H), 4.60 (t, *J*=2.4 Hz, 1H), 3.94 (narrow m, 1H), 2.72 (narrow m,

1H), 2.50 (d, *J*=4.7 Hz, 1H), 2.42 (s, 3H), 2.17 (d, *J*=10.1 Hz, 1H), 1.68-1.57 (m, 1H), 1.47 (d, *J*=10.0, 1H), 1.42-1.14 (m, 2H), 1.08-0.95 (m, 1H). ^{13}C NMR: δ 198.0 (C_8), 144.1 (C_9), 134.2 (C_{12}), 129.4 (C_{10}), 128.6 (C_{11}), 62.4 (C_2), 61.5 (C_3), 47.0 (C_1), 42.7 (C_4), 38.0 (C_7), 26.3 (C_6), 23.1 (C_5), 21.6 (C_{13}). MS: *e/z* (relative intensity) 250 (1.4, M^+), 248 (4.3, M^+), 235 (1.3), 233 (4.0), 213 (11), 183 (5), 181 (15), 119 (100), 91 (56), 65 (16). Anal. Found: C, 72.29; H, 7.01. $C_{15}H_{17}ClO$ calc.: C, 72.42; H, 6.84.

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