dried (Na_2SO_4), evaporated, and recrystallized from ethanol to give 6.0 g (51%): mp 79–80 °C; NMR ($CDCl_3$) 1.46 (m, 2 H), 2.48 (m, 5 H), 4.92 (s, 1 H), 7.22–8.08 (m, 10 H). Anal. C, H.

2-Hydroxy-1-(4-methylphenyl)-2-phenyl-1-ethanone was prepared using published procedures.[20,21] Trimethylsilyl cyanide (4.96 g, 50.0 mmol) was added to 4.78 g (45.0 mmol) of benzaldehyde with stirring. After the mixture cooled, 25 mL of methylene chloride was added and the solution allowed to stir overnight. A Grignard reagent was prepared in the usual manner by combining 8.55 g (50.0 mmol) of *p*-bromotoluene, 1.34 g (55.0 mmol) of magnesium, and 75 mL of absolute ether and adding this mixture to the methylene chloride solution. The mixture was stirred for 2 h and then poured onto 500 g of ice and 20 mL of sulfuric acid. The aqueous layer was allowed to stand overnight and then filtered to collect the crystals that deposited during that time. The ether layer was evaporated and taken up with 75 mL of methanol with 1 mL of 10% aqueous HCl and was also allowed to stand overnight. The solvent was removed, and the resulting solid and the crystals above were recrystallized three times from methanol and water to afford 6.1 g (64%), mp 103–4 °C (lit. mp 109[22] °C).

2-Morpholino-2-phenyl-1-(4-methylphenyl)-1-ethanone was prepared by adding 3.0 g of the previously prepared product to 10 mL of DMF and was treated with 1.4 mL of thionyl chloride under nitrogen. The mixture was stirred for 3 h and then treated with 10 mL of water and 10 mL of methylene chloride. The methylene chloride layer was washed (3 × 10 mL) with water and dried ($MgSO_4$). Rotary evaporation afforded a clear oil (the corresponding chloride), which was used without further purification by dissolving it in 20 mL of anhydrous ether and 7 mL of morpholine and allowing it to stir overnight. Water (20 mL) was added, and the ether layer was washed three times with 20 mL of water, dried (K_2CO_3), evaporated to an oil, and subjected to high vacuum. The oil was identified as nearly pure product (3.3 g, 84%) by NMR and GC–MS spectroscopy. Additional purification by thick-layer chromatography on silica gel afforded a noncrystalline colorless oil, which was pure by NMR, HPLC, and GC–MS analysis: NMR ($CDCl_3$) 1.86 (s, 3 H), 2.30–2.50 (m, 4 H), 3.51–3.66 (m, 4 H), 4.75 (s, 1 H), 6.73–7.04 (m, 5 H), 7.42 (d, J = 6 Hz, 2 H), 7.97 (d, J = 6 Hz, 2 H).

Irradiation of 2b with 9,10-Diethoxyanthracene. A solution of **2b** (6.1×10^{-3} M) and 9,10-diethoxyanthracene (6.4×10^{-3} M) in benzene-d_6 was irradiated as described above. NMR and GC–MS analysis indicated a 55% yield of **8b** along with smaller amounts of unidentified products.

Irradiation of 2b with Tributyltin Hydride. A solution of **2b** (1.5×10^{-3} M) and tributyltin hydride (3.0×10^{-3} M) was prepared as indicated above and allowed to stand in the dark for 5 days. NMR and GC–MS analysis indicated a 49% conversion to **8b**.

Acknowledgment. We thank the National Science Foundation Science and Technology Center for Photoinduced Charge Transfer (Grant CHE 9120001) and the Department of Energy (Grant Number DE-FG02-86ER 13504) for support of this research.

Registry No. 1, 1217-45-4; **2a**, 127029-79-2; **2b**, 794-05-8; **3a**, 63833-44-3; **4a**, 104-87-0; **5**, 100-52-7; **6a**, 1468-28-6; **7a**, 2431-00-7; **7b**, 134-81-6; **8a**, 2001-28-7; **8b**, 451-40-1; 2-hydroxy-1-(4-methylphenyl)-2-phenyl-1-ethanone, 2431-23-4; 2-chloro-1-(4-methylphenyl)-2-phenyl-1-ethanone, 41104-54-5.

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Crystal Structures of Two Activated Cyclohexanones with Opposite Pyramidalizations of the Carbonyl Groups

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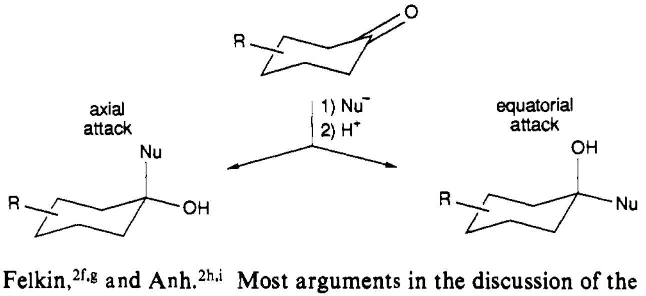
Received February 10, 1992. Revised Manuscript Received July 21, 1992

Abstract: The crystal structure analyses of the two 3,3,5,5-tetraalkylcyclohexanones **1** and **2** activated by Li^+ or $SbCl_5$ complexation show that **1** and **2** have rather different chair conformations and opposite pyramidalizations of the carbonyl group. The bicyclic ketone **1** has an exocyclic C═C double bond acting as an intramolecular nucleophile attacking the carbonyl group from the axial direction, whereas **2** is preferentially attacked by nucleophiles from the equatorial direction. In **1**, the axial α protons (but not the C_α—C_β bonds) are well aligned for hyperconjugative interactions with the carbonyl group, whereas, in **2**, both the axial C_α—H and the C_α—C_β bonds may interact with the carbonyl group. In all structures, a C═O elongation and a $C_{C=O}$—C_α shortening are observed. In addition, **2** shows a slight C_α—C_β elongation. The conformational differences between **1** and **2** are in agreement with the general conformational flexibility of cyclohexanones, as could be shown by comparison of their Cremer–Pople puckering parameters with those of cyclohexanones from the Cambridge Structural Database. The direction of the carbonyl pyramidalization is compared with that of pyramidalized sp^2 C atoms in a norbornenyl cation and discussed in terms of preferential attacks of nucleophiles, as predicted by current models of stereoselective nucleophile addition (Cieplak, Houk, Klein, Felkin).

The explanation of diastereoselective additions of nucleophiles (Nu$^-$) to cyclohexanones (Scheme I) was in recent years the topic of several publications, especially by Cieplak,[1] Houk,[2a–c] Klein,[2d,e] Felkin,[2f,g] and Anh.[2h,i] Most arguments in the discussion of the kinetically controlled additions stem from the interpretation of product ratios[1,2] and the computation of transition states.[2,3]

Scheme I



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[1] (a) Cieplak, A. S. *J. Am. Chem. Soc.* **1981**, *103*, 4540–4552. (b) Cieplak, A. S.; Tait, B. D.; Johnson, C. R. *J. Am. Chem. Soc.* **1989**, *111*, 8447–8462.

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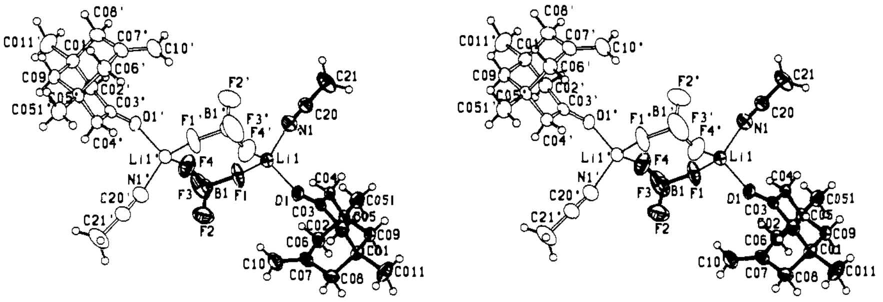


Figure 1. ORTEP stereo drawing of the crystal structure of [(**1**)$_2$·2CH$_3$CN·2LiBF$_4$]. The atoms of the symmetry-related (1 - *x*, 1 - *y*, −*z*) asymmetric unit are drawn as white ellipsoids and have primed labels. The displacement ellipsoids are drawn at the 50% probability level, and the hydrogen atoms are represented by spheres with a radius of 0.1 Å.

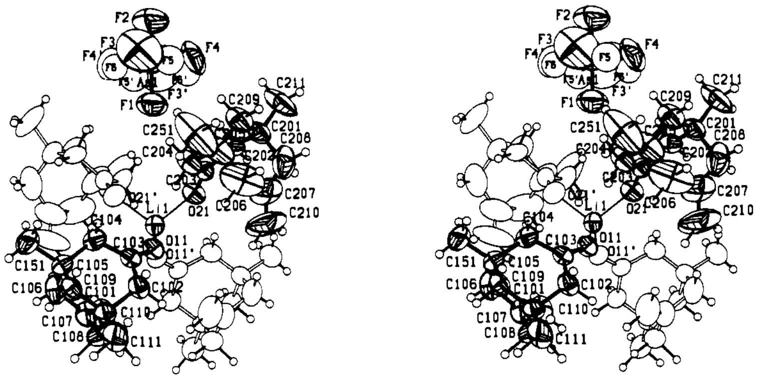
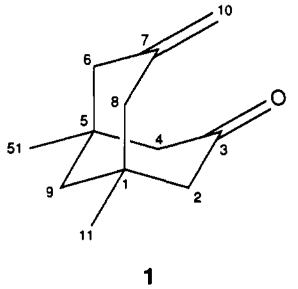
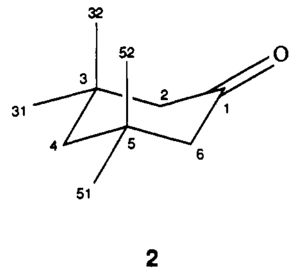


Figure 2. ORTEP stereo drawing of the crystal structure of [(**1**)$_4$·Li]AsF$_6$. The crystallographic C_2 axis passes through the atoms Li1, As1, F1, and F2. Symmetry-related atoms (2 - *x*, *y*, 0.5 - *z*) have primed labels and are drawn as white ellipsoids. The anion is rotationally disordered about the crystallographic C_2 axis. The atoms of the major orientation (F3 and F4; *p* = 0.75) could be refined anisotropically; those of the minor orientation (F5 and F6; *p* = 0.25) could only be refined isotropically. The displacement ellipsoids and the spheres of F5 and F6 are drawn at the 50% probability level; the hydrogen atoms are represented by spheres with a radius of 0.1 Å.

Because of the lack of experimental structure information about activated cyclohexanones, which are reactive intermediates in the course of the additions (most nucleophilic reagents used in the additions contain metal cations, like LiAlH$_4$, NaBH$_4$, NaH, and CH$_3$MgX, or the cyclohexanones are complexed with additional Lewis acids before the nucleophile is added[4]), we carried out crystal structure analyses of the two rather similar cyclohexanones **1** and **2** in complexed form and compares their structural features with those of nonactivated cyclohexanones from the literature.



1

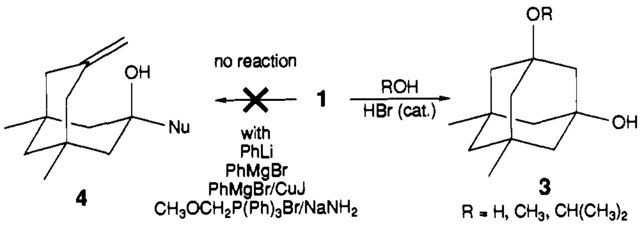


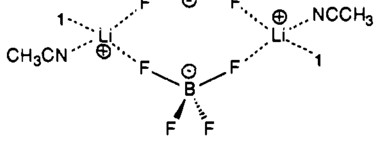
2

Results

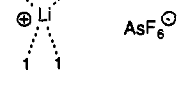
The bicyclic ketone **1** was synthesized in analogy to literature procedures (see Experimental Part). It serves as an example for the pure axial attack, because the olefinic double bond behaves like an intramolecular nucleophile or it prevents the equatorial attack of other nucleophiles, as can be shown by cyclization to the adamantane derivative **3** or by attempted reactions with organolithium, organocopper, Grignard, or Wittig reagents to obtain **4** (see Scheme II). Therefore, a complex of **1** with a metal salt containing a nonnucleophilic and nonbasic counterion (in order to prevent equatorial attack or deprotonation) should yield a good model for a reactive species on the reaction path of an axial attack. We could obtain single crystals suitable for an X-ray structure determination by complexation of **1** with LiBF$_4$ (and addition of acetonitrile). The structure of the centrosymmetric dimeric complex [(**1**)$_2$·2CH$_3$CN·2LiBF$_4$] in the crystal is shown in Figure 1. The cyclic arrangement of two ion pairs is quite often observed in metal–organic chemistry.[5] A crystalline solvent-free complex of **1** was obtained by dissolving LiAsF$_6$ in an excess of pure **1** and subsequent slow cooling and recrystallization. The resulting complex [(**1**)$_4$·Li]AsF$_6$ is situated on a crystallographic C_2 axis

Scheme II





[(1)$_2$·2CH$_3$CN·2LiBF$_4$]



[(1)$_4$·Li]AsF$_6$

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Table I. Selected Bond Angles (Å), Pyramidalizations (Å), Bond Angles (deg), Angles between Planes (deg), and Torsion Angles (deg) of $[(\mathbf{1})_2\cdot 2CH_3CN\cdot 2LiBF_4]$, $[(\mathbf{1})_4\cdot Li]AsF_6$, and $\mathbf{2}\cdot SbCl_5$[g]

$[(\mathbf{1})_2\cdot 2CH_3CN\cdot 2LiBF_4]$		$[(\mathbf{1})_4\cdot Li]AsF_6$: molecule no. x			$\mathbf{2}\cdot SbCl_5$	
			$x = 1$	$x = 2$		
C03–O1	1.229 (5) [1.232]	Cx03–Ox1	1.220 (7) [1.225]	1.197 (7) [1.210]	C1–O1	1.260 (5) [1.263]
C02–C03	1.503 (7) [1.509]	Cx02–Cx03	1.485 (9) [1.501]	1.496 (9) [1.523]	C1–C2	1.499 (6) [1.502]
C03–C04	1.487 (5) [1.492]	Cx03–Cx04	1.50 (1) [1.507]	1.493 (7) [1.520]	C1–C6	1.470 (5) [1.473]
C01–C02	1.531 (5) [1.536]	Cx01–Cx02	1.55 (1) [1.560]	1.53 (1) [1.548]	C2–C3	1.547 (5) [1.551]
C04–C05	1.529 (5) [1.534]	Cx04–Cx05	1.53 (1) [1.538]	1.56 (1) [1.583]	C5–C6	1.565 (5) [1.569]
C07–C10	1.349 (7) [1.354]	Cx07–Cx10	1.326 (9) [1.324]	1.31 (1) [1.325]		
C03···C07	2.913 (5)	Cx03···Cx07	2.88 (1)	2.90 (1)		
C03···C10	3.356 (7)	Cx03···Cx10	3.255 (9)	3.28 (1)		
C06···C08	2.522 (7)	Cx06···Cx08	2.51 (2)	2.51 (2)	C32···C52	3.272 (7)
O1···Li1	1.928 (9)	Ox1···Li1	1.956 (8)	1.94 (1)	O1···Sb1	2.148 (4)
$\lvert\Delta C03\rvert^a$	ax: 0.035 (4)	$\lvert\Delta Cx03\rvert^a$	ax: 0.027 (5)	ax: 0.040 (6)	$\lvert\Delta C1\rvert^a$	eq: 0.011 (4)
$\lvert\Delta C07\rvert^a$	0.015 (5)	$\lvert\Delta Cx07\rvert^a$	0.044 (8)	0.06 (1)		
O1–C03–C02	120.0 (4)	Ox1–Cx03–Cx02	121.4 (6)	122.6 (6)	O1–C1–C2	117.3 (3)
O1–C03–C04	122.0 (5)	Ox1–Cx03–Cx04	122.1 (5)	121.6 (6)	O1–C1–C6	125.2 (4)
C02–C03–C04	117.9 (4)	Cx02–Cx03–Cx04	116.5 (6)	115.5 (5)	C2–C1–C6	117.5 (3)
C03–O1···Li1	132.9 (4)	Cx03–Ox1···Li1	138.7 (4)	133.6 (5)	C1–O1···Sb1	143.2 (3)
$\Psi_1{}^b$	31.5 (3)	$\Psi_1{}^b$	35.4 (5)	35.2 (5)	$\Psi_1{}^c$	52.8 (3)
$\Psi_4{}^d$	54.0 (3)	$\Psi_4{}^d$	54.6 (5)	56.1 (6)	$\Psi_4{}^e$	45.7 (4)
O1–C03–C02–C01	149.8 (5)	Ox1–Cx03–Cx02–Cx01	−144.1 (6)	−146.9 (7)	O1–C1–C2–C3	−118.5 (4)
O1–C03–C04–C05	−149.4 (5)	Ox1–Cx03–Cx04–Cx05	143.9 (6)	144.7 (7)	O1–C1–C6–C5	122.5 (5)
O1–C03–C02–$H2_{ax}$	−85 (3)	Ox1–Cx03–Cx02–$Hx2_{ax}$	97 (4)	*f*		*f*
O1–C03–C04–$H4_{ax}$	85 (3)	Ox1–Cx03–Cx04–$Hx4_{ax}$	−97 (4)	*f*		*f*
O1–C03–C02–$H2_{eq}$	20 (2)	Ox1–Cx03–Cx02–$Hx2_{eq}$	−20 (4)	*f*		*f*
O1–C03–C04–$H4_{eq}$	−21 (2)	Ox1–Cx03–Cx04–$Hx4_{eq}$	18 (4)	*f*		*f*
C02–C03–O1···Li1	174.6 (5)	Cx02–Cx03–Ox1···Li1	161.3 (6)	−170.8 (5)	C2–C1–O1···Sb1	−173.8 (4)
C04–C03–O1···Li1	−0.2 (8)	Cx04–Cx03–Ox1···Li1	−23 (1)	3 (1)	C6–C1–O1···Sb1	7.9 (8)

[a] |ΔA| is the absolute value of the distance of the trivalent atom A from the plane through its three bonding partners; for carbonyl C atoms, "ax" means axial and "eq" means equatorial pyramidalization (see Chart I). [b] Angle between the plane through the C atoms 2, 3, and 4 and the plane through the C atoms 1, 2, 4, and 5 (see Chart I). [c] Angle between the plane through the C atoms 1, 2, and 6 and the plane through the C atoms 2, 3, 5, and 6 (see Chart I). [d] Angle between the plane through the C atoms 1, 5, and 9 and the plane through the C atoms 1, 2, 4, and 5 (see Chart I). [e] Angle between the plane through the C atoms 3, 4, and 5 and the plane through the C atoms 2, 3, 5, and 6 (see Chart I). [f] The corresponding H atoms could only be refined with constraints. [g] Each row contains comparable parameters from the different structures. The values in square brackets are corrected for libration of the isolated ketone molecule.

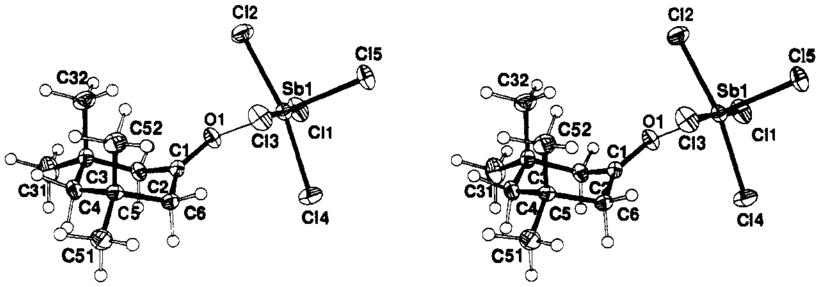

Figure 3. ORTEP stereo drawing of the crystal structure of $\mathbf{2}\cdot SbCl_5$. The displacement ellipsoids are drawn at the 50% probability level, and the hydrogen atoms are represented by spheres with a radius of 0.1 Å.

(see Figure 2). Because the Li^+ ion is complexed by four ketone molecules, there is no space for a fifth coordination partner, and accordingly the crystal is composed of the discrete ions $[(\mathbf{1})_4\cdot Li]^+$ and AsF_6^-. The AsF_6^- ion is rotationally disordered, and the large displacement ellipsoids of several atoms of the ketone molecule no. 2 indicate an orientational disorder (the ellipsoids may be explained by a large-amplitude libration of a rigid body; see the results of the thermal motion analyses in the Experimental Part). The most characteristic structural data of the ketone molecules **1** in both structures are given in Table I.

From the work of Eliel et al.[6] it is known that nucleophiles (like H^- in the reaction with $LiAlH_4$) attack **2** with high preference from the equatorial direction. Because **2** is rather similar to **1** concerning the substituents of the cyclohexanone ring, we carried out the crystal structure analysis of $\mathbf{2}\cdot SbCl_5$ as a model for a preferred equatorial attack.[7] This complex has a structure rather than similar to other complexes of ketones and $SbCl_5$[8] (see Figure 3). The most important structural data are included in Table I. The feature common to all the structures is the lengthening of the C═O bond and the shortening of the $C_{C=O}$—C_α bonds induced by the Lewis acid complexation (we exclude molecule no. 2 of $[(\mathbf{1})_4\cdot Li]AsF_6$ from the discussion because of the large displacement ellipsoids). Compared to the average lengths of these bonds in free ketone molecules[9] (1.210 and 1.511 Å), one finds

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(7) $\mathbf{1}\cdot SbCl_5$ decomposes during the attempted crystallization.

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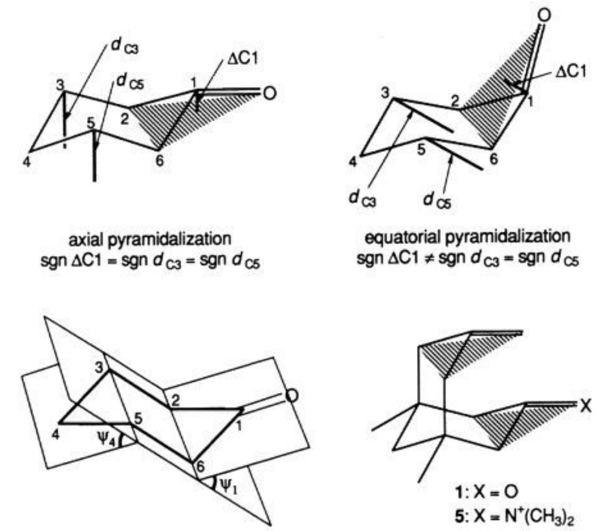
Chart I



axial pyramidalization
sgn $\Delta C1$ = sgn d_{C3} = sgn d_{C5}

equatorial pyramidalization
sgn $\Delta C1 \neq$ sgn d_{C3} = sgn d_{C5}

1: X = O
5: X = $N^+(CH_3)_2$

significant C=O elongations of 0.019 (5) [0.022] Å for $[(\mathbf{1})_2 \cdot 2CH_3CN \cdot {}_2LiBF_4]$ and of 0.050 (5) [0.053] Å for $\mathbf{2} \cdot SbCl_5$[10] and significant average $C_{C=O}$–C_α shortenings of 0.016 (3) [0.010] Å for $[(\mathbf{1})_2 \cdot 2CH_3CN \cdot {}_2LiBF_4]$ and of 0.026 (5) [0.023] Å for $\mathbf{2} \cdot SbCl_5$.[10] The average C_α–C_β bond in $\mathbf{2} \cdot SbCl_5$ is lengthened by 0.018 (3) [0.022] Å, if compared with an average $(R_3C)_3C$–CH_2R bond[9] (1.538 Å). The carbonyl groups are slightly pyramidal in all complexed cyclohexanones. In the three different molecules of **1**, the pyramidalization is axially oriented, whereas it is equatorially oriented in **2** (see Table I and Experimental Part). The olefinic carbon atom 7 is also in all molecules of **1** slightly pyramidal in such a way that the exocyclic C atom 10 approaches the carbonyl C atom (the same distortions were observed in the iminium ion **5**;[11] see Chart I). The two axial methyl groups in $\mathbf{2} \cdot SbCl_5$ are repelling each other, so that the C32⋯C52 distance is 3.272 (7) Å compared to the C06⋯C08 distance in the different complexed molecules **1** (about 2.52 Å). The cyclohexanone ring itself has in all molecules a chair conformation, but the region around the carbonyl group is more flat in **1** and more puckered in **2**, as shown by Ψ_1 = 31.5 (3) - 35.4 (5)° for **1** and 52.8 (3)° for **2**, (see Table I) in comparison with Ψ_1 = 38.2° for an uncomplexed cyclohexanone like 4,4-diphenylcyclohexanone.[12] For the C4 tip, the opposite distortion is observed: Ψ_4 has a value between 54.0 (3) and 56.1 (6)° in complexed **1** and a value of 45.7 (4)° in $\mathbf{2} \cdot SbCl_5$, whereas in 4,4-diphenylcyclohexanone[12] it has a value of 51.7°. A consequence of the different angles Ψ_1 in the complexes of **1** and **2** is the different orientation of the C_α–R (R = C_β, H_{ax}, H_{eq}) bonds with respect to the symmetry axis of the p_C orbital of the carbonyl C atom (see Table I). In those cases, where the C_α protons of **1** could be refined without constraints, the torsion angles $|O{=}C{-}C_\alpha{-}H_{ax}|$ lie in the range 85 (3)–97 (4)°; i.e., the C_α—H_{ax} bonds are synperiplanar with the p_C orbital, and the C_α—C_β bonds form a torsion angle of about 59° with the p_C orbital, whereas, in $\mathbf{2} \cdot SbCl_5$, the C_α—C_β bonds form a torsion angle of about 31° with the p_C orbital. From the calculated $H_{ax}(C_\alpha)$ positions, it follows that the C_α—H_{ax} bonds form a torsion angle of more than 27° with the p_C orbital.

In order to clarify whether the conformational differences between **1** and **2** in the complexes occur only in these molecules or whether they are a general phenomenon also observed in other cyclohexanones and whether or not the conformational differences are due to the complexation,[13] we compare their data with those of other cyclohexanones from the Cambridge Structural Database.[14] Because the six ring atoms of a cyclohexanone have three conformational degrees of freedom, a three-dimensional representation of the different conformers is necessary. We choose the Cremer–Pople puckering parameters[15] q_2, ϕ_2, and q_3, which can be transformed into the spherical coordinates Q, θ, and ϕ, because we thus use the whole set of conformational information for the ring. From a graphical representation of these data, it can be concluded that the conformations and C1 pyramidalizations in our structures agree with a *generally observed correlation between conformational change and the pyramidalization of C1 in the chair family*; i.e., nonactivated cyclohexanones with a chair conformation similar to that of **1** are axially pyramidalized, and those with a chair conformation similar to that of **2** are equatorially pyramidalized (see Supplementary Material).

Because the IR spectra of complexes between ketones and SbF_5 have been intensively studied by Vančik and Sunko[16] in terms of hyperconjugative interactions, we also measured the ^1H and ^{13}C NMR spectra of **2** and $\mathbf{2} \cdot SbCl_5$ at low temperature (see Figure 4).[17] The changes of the ^{13}C chemical shifts upon complexation are similar to those observed for adamantanones:[8] the carbonyl C and the C_β atom are shifted downfield, while the C_α and the C_γ atoms are shifted upfield.

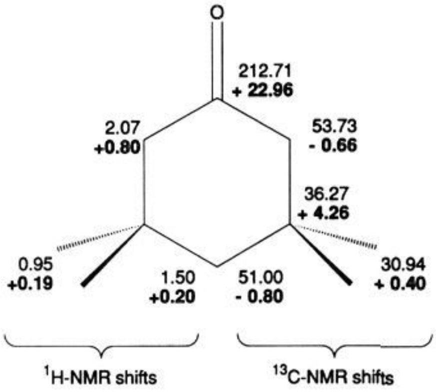
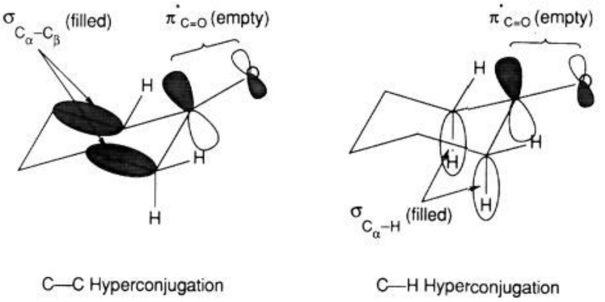


Figure 4. ^1H and ^{13}C NMR chemical shifts in ppm of **2** (upper values) and their changes upon complexation with $SbCl_5$ (lower values, bold) measured at -50 °C in CD_2Cl_2.

Chart II



Discussion

The main effect resulting from the activation of the carbonyl group is the enhanced electrophilicity of the carbonyl C atom.

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(10) Because of the lower precision and the slight disorder in $[(\mathbf{1})_4 \cdot Li]AsF_6$, there are no significant effects detectable.

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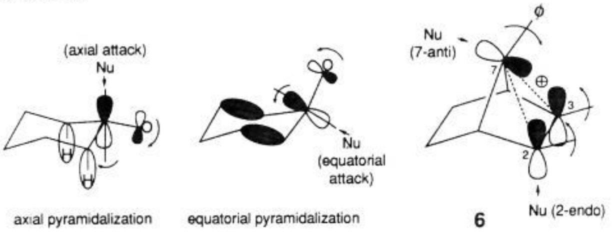
Chart III



axial pyramidalization equatorial pyramidalization **6**

Therefore, one can expect the same electronic effects as in carbocations,[18] where suitably aligned σ and π bonds release electron density toward the empty p orbital, if ordinary π conjugation is not possible (hyperconjugation, σ and π participation). The weaker electrophilicity of activated ketones compared to carbocations results only in hyperconjugative effects; because all C_{α} atoms in **1** and **2** are substituted by H and C, C–H and C–C hyperconjugation are possible (see Chart II). Because of the strong Lewis acidity of $SbCl_5$ and the fact that each Li^+ ion is coordinated to four electron-releasing ligands whereas the $SbCl_5$ is coordinated only to one ketone molecule, stronger effects must be expected for **2**$\cdot SbCl_5$. The average shortening of the $C_{C=O}—C_{\alpha}$ bonds resulting from any hyperconjugation is indeed weaker for **1** and stronger for **2** (0.016 (3) [0.010] vs 0.026 (5) [0.023] Å) compared to the pure ketones. The torsion angles $|O{=}C—C_{\alpha}—H_{ax}|$ about 90° in **1** are ideal for C—H hyperconjugation, whereas the C—C hyperconjugation is strongly disfavored because of $|O{=}C—C_{\alpha}—C_{\beta}|$ between 144 and 150°, and the $C_{\alpha}—C_{\beta}$ bonds in **1** are not significantly lengthened. In **2**, both the $C_{\alpha}—C_{\beta}$ and the calculated $C_{\alpha}—H_{ax}$ bonds are comparably well (but not perfectly) aligned for hyperconjugative interactions ($|O{=}C—C_{\alpha}—C_{\beta}|$ and $|O{=}C—C_{\alpha}—H_{ax}|$ about 120°), and an elongation of $C_{\alpha}—C_{\beta}$ by 0.018 (3) [0.022] Å is observed. These values are very similar to those observed in an activated adamantanone.[8] In this context, the directions of the pyramidalizations in **1** and **2** are striking, because the axial pyramidalization in **1** bends the symmetry axis of the p_C atomic orbital of $\pi_{C=O}{}^*$ toward the $C_{\alpha}–H_{ax}$ bonds acting as electron donors, whereas the equatorial pyramidalization in **2** bends this axis toward the $C_{\alpha}–C_{\beta}$ bonds[19] (force field calculations[20] for uncomplexed **2** predict an *axial* pyramidalization of 0.013 Å) (see Chart III). The structure of the electronically related 1-methyl-1-cyclohexyl cation was interpreted in an analogous way in order to explain NMR data (an axially and an equatorially pyramidalized chair conformer were found).[21] The same kind of pyramidalization of sp^2 C atoms was observed in a much stronger form at the cationic C atoms 2, 3, and 7 in the crystal structure of the 7-norbornenyl cation **6**,[18c] where the former C2–C3 double bond seems to be the most efficient donor (much better than the C7 phenyl ring). The observed nonplanarity of C2, C3, and C7 was explained as the result of the high tendency to maximize the overlap between the p-like orbitals, and the directions of the pyramidalizations are such that the conversion of sp^2 centers into sp^3 centers in the course of a nucleophilic attack (from the 2-endo or the 7-anti direction) can take place in agreement with the principle of least motion.[22] The directions of the pyramidalizations in complexed **1** and **2** seem to follow the same principle: **1** is axially pyramidalized, and the nucleophilic attack of the C7=C10 bond is axial, while **2** (equatorially pyramidalized) is preferentially attacked by nucleophiles from the equatorial direction.[23] We assume in this discussion that the transition states of the (kinetically controlled) nucleophilic additions to an activated ketone[2f,g] or to a carbocation are structurally and energetically similar to these reactive intermediates (early transition state; Hammond postulate), although the reactive intermediates are electron-deficient, while the transition states are more electron rich because of the involved nucleophile.

It must be emphasized that our experimental data are also in agreement with the following rules and predictions: (a) the correlation of the direction of the carbonyl pyramidalization in complexed **1** and **2** with the direction of the preferred nucleophile attack corresponds with Houk's observations and calculations;[23] (b) the correlation of the arrangement of the $C_{\alpha}–R$ bonds in complexed **1** and **2** with the preferred nucleophile attack agrees with the Felkin model[2f,g] (the cyclohexanone ring of **1** is attacked from the axial direction, because an equatorial attack would result in a high "torsional strain" of the nucleophile with the $C_{\alpha}–H_{ax}$ bonds; **2** is attacked from the equatorial direction, because an axial attack would result in "steric strain" with the C32 and C52 methyl groups); (c) the slight shortenings of the $C_{C=O}—C_{\alpha}$ bonds and the elongation of the $C_{\alpha}—C_{\beta}$ bonds (only in **2**) agree in principle with the electronic interaction between the $C_{\alpha}–R$ σ bond orbitals and the C=O π orbitals or the incipient C—Nu σ orbitals suggested by Klein[2d,e] and proposed to be operative in the transition state of the nucleophile (Nu) addition by Cieplak.[1a]

Conclusion

The electronic effects concerning the interaction between the carbonyl group and $C_{\alpha}–C_{\beta}$ or $C_{\alpha}–H$ bonds suggested by Houk, Felkin, Klein, and Cieplak for the activated carbonyl compounds or the transition states of the nucleophile addition are consistent with the observed structures of activated cyclohexanones. The actual conformation of any other cyclohexanone and the therewith correlated direction of the pyramidalization (and the related direction of a nucleophilic attack), however, may be influenced by the substituents of the ring and are difficult to predict.

Experimental Part

Synthesis of 1,5-Dimethyl-7-methylenebicyclo[3.3.1]nonan-3-one (1). The ketone **1** was synthesized starting from commercially available 3,5-dimethyladamantan-1-ol as follows: bromination with HBr/glacial acetic acid,[24] Koch–Haaf reaction, and bromination with $Br_2/AlBr_3$[25] to give 3-bromo-5,7-dimethyladamantane-1-carboxylic acid, followed by conversion to the amide and Hofmann degradation to a urethane, from which ketone **1** is obtained by refluxing in aqueous sodium hydroxide for 60 h.[26] ^{1}H-NMR (300 MHz, $CDCl_3$), δ(ppm): 4.74 (t, $C(10)H_2$, G); 2.20 (d × d, $C(2,4)H_{eq}$, Y), 2.08 (d × d, $C(6,8)H_{eq}$, N); 1.98 (m, $C(2,4)H_{ax}$, X); 1.97 (m, $C(6,8)H_{ax}$, M); 1.60 (t × d, $C(9)H_{ax}$,[27] A); 1.51 (t × d, C-$(9)H_{eq}$,[27] B); 1.05 (s, 2 CH_3); $J_{AB} = 13.2$ Hz, $J_{MN} = 13.5$ Hz, $J_{XY} = 16.6$ Hz, $J_{AN} = 2.2$ Hz, $J_{BY} = 2.5$ Hz, $J_{MG} = 1.8$ Hz, $J_{MX} = 1.5$ Hz. ^{13}C NMR (75 MHz, $CDCl_3$), δ(ppm): 210.9 (C3); 142.8 (C7); 114.0 (C10);

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(19) We considered the carbonyl pyramidalization in 5-phenyladamantanone$\cdot SbCl_5$ (ref 8, footnote 14) as meaningless because of two significantly different $C_{\alpha}—C{=}O$ angles. Such a distortion occurs also in **2**$\cdot SbCl_5$ (see Table I). It may be possible that the pyramidalization in 5-phenyladamantanone (equatorial with respect to the ring containing C5, axial with respect to that containing C7) was significant; in that case, the direction of the pyramidalization does not agree with the explanation of the stereoselectivity given by: Cheung, C. K.; Tseng, T. L.; Lin, M.-H.; Srivastava, S.; le Noble, W. *J. Am. Chem. Soc.* **1986**, *108*, 1598–1605. The direction of the observed pyramidalization in 5-phenyladamantanone is consistent with the effect mentioned in ref 8, footnote 15.

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(27) The positions of the C9 protons refer to the cyclohexanone ring.

Table II. Data about the Crystal Structure Analyses

compd	$[(\mathbf{1})_2\cdot 2CH_3CN\cdot 2LiBF_4]$	$[(\mathbf{1})_4\cdot Li]AsF_6$	$\mathbf{2}\cdot SbCl_5$
space gp (no.)	$P2_1/c$ (14)	$C2/c$ (15)[a]	$Pna2_1$ (33)[b]
a (Å)	8.042 (9)	15.282 (9)	20.811 (6)
b (Å)	27.933 (6)	25.509 (6)	12.451 (3)
c (Å)	8.574 (8)	14.162 (4)	6.270 (5)
α (deg)	90	90	90
β (deg)	119.41 (9)	116.57 (4)	90
γ (deg)	90	90	90
V (Å^3)	1678 (3)	4938 (4)	1625 (1)
measuring temp (°C)	−80	−40	−80
d_X (g·cm^{-3})	1.239	1.223	1.853
θ_{max} (deg)	25	25	40
no. of measured reflections	2941	4543	6831
no. of reflections with $I > n\sigma_I$; n	1851; 3	1897; 3	4806; 5
no. of parameters	279	345	154
w	$1/\sigma_F^2$	$1/\sigma_F^2$	$1/\sigma_F^2$
R	0.055	0.056	0.041
R_w	0.051	0.051	0.053
μ (cm^{-1})	1.001	7.443	25.236

[a] Because of severe correlations, the structure could not be refined in the space group *Cc*. [b] The space group *Pnma* can be excluded because of lack of symmetry in the complex.

53.1 (C2,4); 47.8 (C6,8); 47.3 (C9); 34.8 (C1,5); 30.3 (2 CH$_3$).

Synthesis and Crystallization of $[(\mathbf{1})_2\cdot 2CH_3CN\cdot 2LiBF_4]$. A solution of 601 mg of ketone **1** in 6 mL of CH$_2$Cl$_2$ was slowly added to a suspension of 316 mg LiBF$_4$ and 2 mL of CH$_2$Cl$_2$ at room temperature (RT) under argon. After the reaction mixture was stirred for 2 h, 2 mL of CH$_3$CN was added while the reaction mixture was cooled to 10 °C and stirred again for 15 min. After filtration under argon, the solution was slowly cooled to −80 °C, starting at 10 °C. The resulting colorless crystals were dried for 10 min under high vacuum after removal of the mother liquor and washing with 2 mL CH$_2$Cl$_2$.

Synthesis and Crystallization of $[(\mathbf{1})_4\cdot Li]AsF_6$. In 2.5 mL of the ketone **1** was dissolved 86 mg of LiAsF$_6$ at 110 °C under argon. The solution was cooled to RT, yielding very fine needles of the product. To obtain suitable crystals, these needles were dissolved again at 70 °C, and while cooling the solution to RT, some seed crystals were added. The resulting colorless crystals were washed several times with pentane.

Synthesis and Crystallization of $\mathbf{2}\cdot SbCl_5$. To a solution of 335 mg of **2** in 30 mL of CFCl$_3$ was slowly added a solution of 649 mg of SbCl$_5$ in 6 mL of CCl$_2$FCClF$_2$ at −80 °C under argon. After the solution was stirred for 30 min, the solvents were removed under high vacuum and the complex was dissolved in 20 mL of CH$_2$Cl$_2$ at −30 °C. After filtration, the solution was slowly cooled to −80 °C. The resulting brownish crystals were dried for 10 min under high vacuum after removal of the mother liquor.

NMR Measurements of $\mathbf{2}\cdot SbCl_5$. About 30 mg of recrystallized $\mathbf{2}\cdot SbCl_5$ was added to an NMR tube under inert gas and dissolved in CD$_2$Cl$_2$ at low temperature (no internal standard was added, the reference was CD$_2$Cl$_2$). The ^{1}H and ^{13}C NMR spectra were recorded at −50 °C. The spectrum of the pure ketone **2** was measured under identical conditions.

X-ray Crystal Structure Determinations. All structures were measured on an Enraf-Nonius CAD4 diffractometer (Mo K$_\alpha$ radiation, graphite monochromator; for the crystal data see Table II). The structure of $[(\mathbf{1})_2\cdot 2CH_3CN\cdot 2LiBF_4]$ was solved by the direct method option; and the heavy atoms of $[(\mathbf{1})_4\cdot Li]AsF_6$ and $\mathbf{2}\cdot SbCl_5$ (As, Sb) were determined with the Patterson option of SHELXS-86.[28] The remaining non-hydrogen atoms were located by a difference Fourier synthesis with SHELX-76.[29] After several cycles of isotropic and anisotropic refinement and subsequent location of hydrogen positions, the following hydrogen atoms were refined with the constraints shown.

$[(\mathbf{1})_2\cdot 2CH_3CN\cdot 2LiBF_4]$: H212 fixed (C21–H212 = 1.000 Å, C20–C21–H212 = 109°, N1–C20–C21–H212 = 12°).

$[(\mathbf{1})_4\cdot Li]AsF_6$: Molecule no. 1, H101 and H102 fixed at the calculated positions and U fixed at U_{equiv} of the corresponding C atom; molecule no. 2, H201 and H202 fixed at the calculated positions and all other H's riding and all U's fixed at U_{equiv} of the corresponding C atom.

$\mathbf{2}\cdot SbCl_5$: All H's riding and U's fixed at $1.2U_{equiv}$ of the corresponding C atom; the computed C32 and C52 hydrogen positions are probably not correct with regard to a rotation around the C3–C32 or C5–C52 bond.

The refinements of $[(\mathbf{1})_2\cdot 2CH_3CN\cdot 2LiBF_4]$ and $\mathbf{2}\cdot SbCl_5$ were completed in the Xtal 3.0 system.[30] An extinction correction according to Becker and Coppens (Gaussian distribution) was applied and refined in the last cycles of the refinement of $\mathbf{2}\cdot SbCl_5$ with CRYLSQ[30,31] (ρ = 1.74 (9)). Other options for the extinction correction with CRYLSQ gave slightly worse R values. An extinction correction with the simpler extinction model in SHELX-76 gave an equatorial pyramidalization with $|\Delta C1|$ = 0.019 (5) Å (see Table I). In no case was the direction of the C1 pyramidalization inverted.

The crystallographic figures (1–3) were drawn with ORTEP.[32] The large displacement ellipsoids of $[(\mathbf{1})_4\cdot Li]AsF_6$ can be explained by separate thermal motion analyses of the two ketone molecules (both treated as rigid bodies) using THMA11[33] (roots of the eigenvalues of the **T** and **L** tensors and weighted R's for all U's: molecule no. 1 0.24 Å, 0.23 Å, 0.21 Å, 7.56°, 3.34°, 3.16°, R = 0.103; molecule no. 2 0.29 Å, 0.23 Å, 0.19 Å, 10.4°, 7.4°, 4.2°, R = 0.074). $[(\mathbf{1})_4\cdot Li]AsF_6$ decomposed during the X-ray measurement; the intensity of the control reflections decreased to 70%. Because of a beginning phase transition from monoclinic to triclinic at −80 °C, the structure was measured at −40 °C.

Acknowledgment. We thank Brigitte Brandenberg and Privatdozent Dr. Bernhard Jaun for the NMR measurements and Dr. Engelbert Zass for several CAS online searches. Financial support from the Schweizerischer Nationalfonds is acknowledged. The Fonds der Chemischen Industrie (Federal Republic of Germany) sponsored the work by the allocation of a Dozentenstipendium to T.L.

Supplementary Material Available: Crystal packing diagrams; tables of the positional and thermal parameters and of the bond lengths, angles, torsion angles, and contact distances; discussion, listings, and graphical representations of the puckering parameters (55 pages); listings of the observed and calculated structure factors (61 pages). Ordering information is given on any current masthead page.

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