in thickness may be grown from less than 1 g of $Ti[CH_2C(CH_3)_3]_4$ over 6 h. Faster deposition rates and thicker films can be achieved by raising the temperature above 150 °C. Remarkably, upon dissolution of the Pyrex substrate in hydrofluoric acid, the films are cohesive and retain their integrity despite their largely amorphous nature.[14] Previous MOCVD investigations of TiC films have required higher temperatures and more complicated deposition techniques.[15,16] Furthermore, these films were not single-phase TiC, contained substantial amounts of impurities and lacked cohesiveness upon dissolution of the substrate. Adhesive TiC coatings from $Ti[CH_2C(CH_3)_3]_4$ can also be formed on substrates other than Pyrex such as copper and KBr.

The amorphous TiC films are expected to be resistant to the intergranular decohesion and intragranular cleavage characteristic of polycrystalline samples.[17] However, while the hydrocarbon inclusions and defect sites may make the amorphous films less brittle and more suited for certain applications, they also are expected to significantly decrease the hardness of the TiC coatings. Given this trade off between mechanical strength and hardness, it would be of interest to tailor the properties of the TiC films to suit the application at hand while still retaining the advantage of operating at low temperature. We have found that increasing the pressure above 10^{-4} torr without changing the temperature results in the deposition of *crystalline* TiC coatings as revealed by the carbon AES signature and the presence in the electron diffraction micrographs of sharp, well-defined rings located at the proper TiC d spacing. The physical properties of these crystalline deposits appear similar to the hard but brittle TiC films prepared at conventional, high (1100–1350 °C) temperatures.[7] The absence of hydrocarbon inclusions and associated defect sites in the crystalline films may result from collision-induced stripping of the tetraneopentyltitanium molecules of most of their hydrocarbon ligands in the gas phase before reaching the surface.

One possible mechanism for the deposition of the TiC films produced in the present study involves three principal steps: γ-abstraction in $Ti[CH_2C(CH_3)_3]_4$ with loss of neopentane to give titanacyclobutanes, II, loss of isobutylene from the metallacycle to generate titanium methylene species, III, and hydrogen transfer between methylene groups to give methane and titanium carbide, IV. Most of these steps have precedents in the organometallic
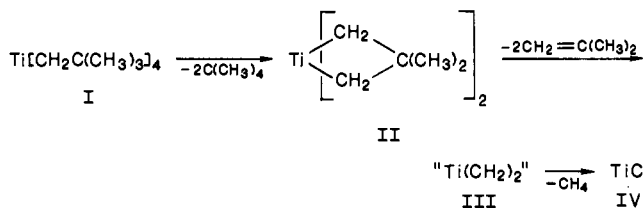
chemistry of early transition metals,[18–21] and neopentane is in fact a product of the thermolysis of $Ti[CH_2C(CH_3)_3]_4$.[9,10] Other mechanisms are, of course, possible and we are currently carrying out labeling studies and complete analyses of the volatile products to determine more precisely the course of the deposition process. One interesting unanswered question is what reactions occur in the gas phase at varying temperatures and pressures before deposition of titanium species on the substrate begins?

These results have shown that TiC films can be obtained by using chemical vapor deposition techniques under very mild conditions. The low temperatures (ca. 150 °C) characteristic of this organometallic route make possible the deposition of TiC films on substrates such as polymers and low-melting metals that are too thermally fragile for other techniques. Extensions of this organometallic route to the synthesis of other early-transition-metal carbides are obvious. Further investigations of refractory coatings are under way; we are particularly interested in the mechanism of the chemical deposition process, the temperature stability and corrosion resistance, and the structure and physics of ordered vs. disordered solids.

The Antiperiplanar Effect in 1,2-Asymmetric Induction

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More than 30 years ago Cram and co-workers formulated a rule for predicting the preferred face of attack by a nucleophile at a carbonyl group adjacent to an asymmetric center.[1] Subsequently, a number of alternate models were put forward by Cornforth,[2] Karabatsos,[3] and Felkin.[4] The four models which represent different rotameric transition states are shown in Figure 1. Later, theoretical calculations by Anh and Eisenstein[5] supported the Felkin model, suitably modified to allow nonperpendicular attack by hydride ion.[6] In arriving at this conclusion, they attributed a key role to the strong energetic preference for an antiperiplanar (app) approach to permit an n–σ* interaction between the pair of electrons of the nucleophile and the σ* antibonding orbital of the antiperiplanar C–L bond.[7] They also compared the relative stabilization energies due to an app C–H, C–C, and C–Cl bond in the transition state for hydride addition. The energies were calculated to be 35.5, 37.4, and 59.0 kcal/mol, respectively (relative to unreacted starting materials). The greater stability of C–C over C–H was attributed to a more favorable n → σ* interaction with the weaker C–C bond (lower energy σ* orbital) and the stabilization by C–Cl to the electronegativity of chlorine. In spite of the fundamental importance of this proposed n–σ* interaction, little theoretical[8] or experimental[9] work has

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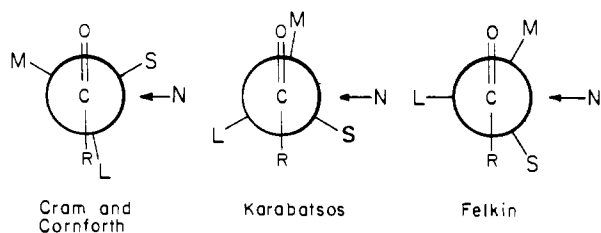
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J. Am. Chem. Soc., Vol. 109, No. 5, 1987 1581

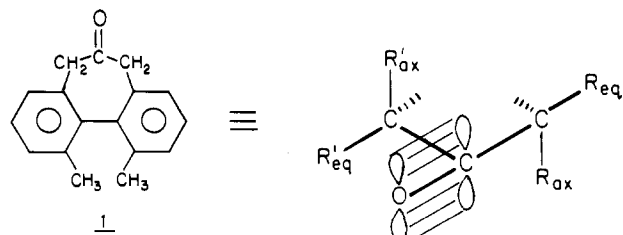**Figure 1.** Models proposed to explain 1,2-asymmetric induction.

Figure 2. Structural and 3-dimensional representation of ketone **1**. Compound **2** has $R_{eq} = CH_3$, compound **3** has $R_{ax} = CH_3$, compound **4** has $R_{ax} = R'_{ax} = CH_3$, and compound **5** has $R'_{eq} = R_{eq} = CH_3$.

Table I. Rate Measurements for Compounds **1–5**[a]

run	$k \times 10^4$	$k' \times 10^4$	rate ratio (k/k')	$\Delta\Delta G^*$
1 (**1** vs. **2**)	$k_1 = 0.55$	$k_2 = 0.11$	5.0	0.9
2 (**1** vs. **3**)	$k_1 = 72.7$	$k_3 = 1.3$	56.0	2.3
3 (**2** vs. **3**)	$k_2 = 10.7$	$k_3 = 1.0$	10.7	1.4
4 (**3** vs. **4**)	$k_3 = 1.0$	$k_4 = 0.54$	1.9	0.4
5 (**4** vs. **5**)	$k_4 = 0.84$	$k_5 = 0.049$	17.1	1.7

[a] All relative rates were measured by using solutions of the ketones (300 mg) in 3 mL of dioxane-dioxane-d_8 (4:1) containing a tenfold excess of $H_2{}^{18}O$ vs. total ketone and a quantity of trifluoroacetic acid sufficient to cause half-lives of at least 30 min for the more rapid exchange. Exchange rates were measured from peak-height ratios for the $C^{16}O$ vs. $C^{18}O$ signals. All rate constants were obtained from treatment of the data by the method of Sachs (*Acta. Chem. Scand.* **1971**, *25*, 3123–3134). The values obtained are accurate to ±5% or less, yielding uncertainties in $\Delta\Delta G^*$ of less than 0.1 kcal/mol. The measurements were recorded by using an XL-300 operating at 75 MHz and at a temperature of 20 °C.

followed. In this paper, we wish to quantify the interaction for C–H vs. C–C bonds by measuring the difference in rates of nucleophilic addition to a carbonyl having a C–H vs. C–methyl bond app to the attacking nucleophile.

For this study, we have selected as a rigid model[10-12] the bridged biaryl ketone **1** whose C_2 axis imparts to it a particular advantage. We have prepared both monomethyl derivatives, **2** and **3**, as well as the $\alpha\alpha'$-diaxial, **4**, and $\alpha\alpha'$-diequatorial, **5**, derivatives. Figure 2 gives a 3-dimensional representation for these compounds. For each of the five ketones, we have measured, pairwise, the relative rates of acid-catalyzed isotopic exchange in the nucleophilic addition of $H_2{}^{18}O$. The uptake of ^{18}O was monitored by ^{13}C NMR, making use of the isotopic shift caused by incorporation of ^{18}O into the carbonyl group of each ketone.[14] The results are sum-

marized in Table I. Compound **2**, having one equatorial methyl, exchanges 5 times more slowly than the parent ketone, **1**. This represents a 0.9-kcal increase in activation energy, presumably due to the development of two vicinal C/O interactions in the geminal diol derived from **2**.[15] These interactions should also be present in the transition state to a slightly diminished extent. The rate of exchange of the axial-methyl derivative, **3**, is far more severely retarded, 56-fold vs. **1**. This larger retardation is not surprising, since the axial derivative, **3**, has a steric interaction with the second aromatic ring and thus will be less able to adjust to increased steric repulsive forces in the transition state.

The observed steric effect in **3** relative to **1** can be seen in the free energy–reaction coordinate diagrams in Figure 3. The free energy profile for **1** is symmetrical, since the faces of its carbonyl are homotopic. In **3**, whose faces are diastereotopic, attack by $H_2{}^{18}O$ will be retarded sterically on either face yet aided, possibly by an n–σ* interaction, when the nucleophile attacks antiperiplanar to the methyl group. Thus, one side of the curve for **3** will have a higher energy transition state than that for **1**, but the other side may benefit from stabilization by the app interaction. Naturally, both barriers must be traversed in an exchange, but only the higher one is observable experimentally. In **4**, however, symmetry is restored to the reaction coordinate (also see Figure 3). Consequently, in exchange of the diaxial derivative **4** the n–σ* stabilizing effect will be present during attack from either side, as will the steric effects at both methyl groups. If we assume the steric effects to be twice as large in **4** as in **3**, the activation energy of **4** will increase by 2S relative to that of **1**, while any app effect should diminish it. Experimentally, the exchanges of **4** vs. **3** and **3** vs. **1** show the transition state for **4** to be 2.3 + 0.4, or 2.7, kcal greater than that for **1**. Thus 2S – app = 2.7 kcal, and since S = 2.3 kcal, the app (n–σ*) effect amounts to 1.9 kcal/mol. This represents a minimal value, as the two steric effects in **4** likely exceed twice the value determined for **3** vs. **1**.[16]

In summary, we have presented evidence that the n–σ* interaction between the nucleophile water[17] and an app C–C bond is at least 1.9 kcal/mol greater than for that with an app C–H bond, a finding consistent with the theoretical calculations of Anh and Eisenstein and the model of Felkin for 1,2-asymmetric induction.

Figure 3. Free energy–reaction coordinate diagrams representing the isotopic exchange reactions of **1**, **3**, and **4**.

(10) This ketone, 4',1''-dimethyl-1,2:3,4-dibenzocyclohepta-1,3-dien-6-one[12] has axial-like and equatorial-like bonds α to the carbonyl (see Figure 2) but possesses much greater rigidity than cyclohexanone. Fraser, R. R.; Champagne, P. J. *Can. J. Chem.* **1976**, *54*, 3809–3811.

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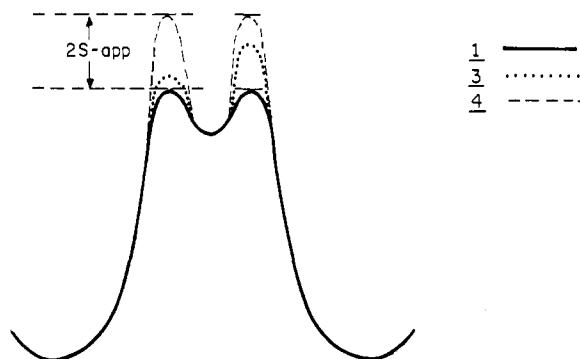
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(16) A comparison of the exchange of **5** vs. **2** and **1** shows the much larger strain in the diequatorial transition state (4.4 kcal/mol) than in the monoequatorial case (0.9 kcal/mol). This excess over additivity is surprisingly high, yet understandable, since each equatorial methyl bisects the adjacent geminal hydroxyl groups. Consequently, any distortion to diminish one gauche interaction will increase the other.

(17) Conceivably, experimental results with water as the nucleophile may not be strictly comparable with the calculations involving hydride ion.