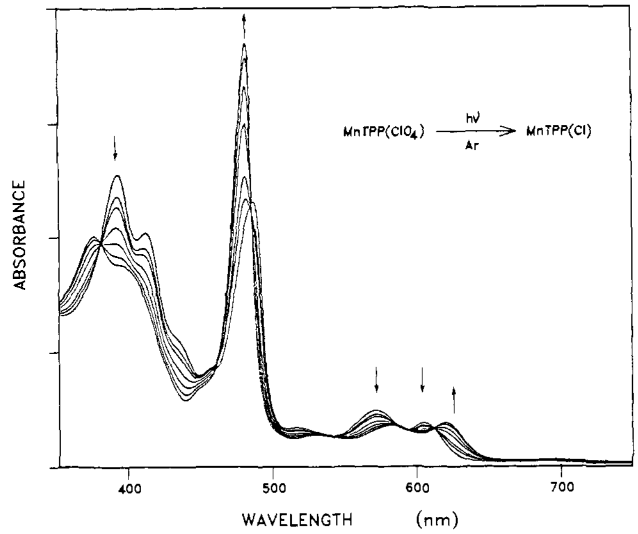

Figure 1. Photolytic conversion of MnTPP(ClO$_4$) to MnTPP(Cl). Arrows indicate the change in absorbance during irradiation. Irradiation of MnTPP(ClO$_4$) in toluene from 310 to 490 nm under Ar produces exclusively MnTPP(Cl) and benzaldehyde.

inverse first order in [OAc].[7] Manganese porphyrins are known *thermal* catalysts for hydrocarbon oxidations with various strong oxidants.[6,8,9] We have examined the product distributions for cyclohexene oxidation and find identical ratios of allylic oxidation to epoxidation for the thermal oxidation with iodosylbenzene and the photooxidations. This similarity strongly suggests that the active oxidizing species is the same in both cases: i.e., a putative O=MnTPP$^+$ complex. Secondary oxidation of initial products occurs in the photocatalytic systems, converting the initially formed alcohols to ketones or aldehydes. These results are consistent with the following partial mechanism.

$$\mathrm{MnTPP(OAc)} + \mathrm{IO_4^-} \rightleftharpoons \mathrm{MnTPP(IO_4^-)} + \mathrm{OAc^-} \qquad (2)$$

$$\mathrm{MnTPP(IO_4^-)} \rightarrow \mathrm{O{=}MnTPP^+} + \mathrm{IO_3^-} \qquad (3)$$

$$\mathrm{O{=}MnTPP^+} + \mathrm{R_3CH} \rightarrow \mathrm{MnTPP^+} + \mathrm{R_3COH}\ \text{etc.} \qquad (4)$$

The photochemical O atom transfer from ClO$_4^-$ or IO$_4^-$ has some precedent in the photocatalytic oxygen atom transfer by chromium porphyrins[10] from *N*-oxides to 1-phenylethane-1,2-diol. In fact, the photolysis of CrTPP(ClO$_4$) produces the stable CrTPP(O) in quantitative yield.[11]

In summary, we have shown that Mn(TPP)ClO$_4$ can be photochemically converted cleanly to Mn(TPP)Cl, resulting in stoichiometric oxidation of organic substrates. This reaction can be extended to truly photocatalytic oxidations simply by using solubilized oxoanions. We believe that under these reaction conditions, higher oxidation state oxo-manganese species are formed, as has been demonstrated in the hydrocarbon oxidations by various active oxidants which manganese porphyrins catalyze. Further work on the elucidation of the mechanism for these reactions is under way.

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(7) Thermal oxidations with IO$_4^-$ were noted but in all cases were very much slower than the photocatalytic ones. Furthermore, in the case of cyclohexene oxidation, the thermal reaction gave almost exclusively allylic oxidation. Slow porphyrin oxidative degradation does occur under the thermal conditions, in the presence of IO$_4^-$. Control reactions run under Ar or O$_2$, in the absence of IO$_4^-$, with or without photolysis, gave no observable oxidation; controls run in the absence of MnTPP(OAc) gave no observable oxidation.

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On the Origin of Diastereofacial Selectivity in Additions to Chiral Aldehydes and Ketones: Trajectory Analysis[1]

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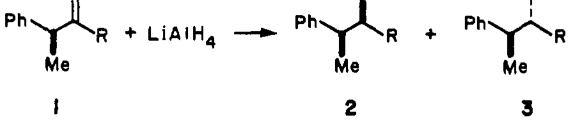
In an earlier communication,[2] we proposed that diastereofacial selectivity in nucleophilic additions to chiral aldehydes might be related to the trajectory of a nucleophile in its attack on the carbonyl group (Figure 1). This argument provides a tidy explanation of the observation by Chērest, Felkin, and Prudent that asymmetric induction increases markedly in the series of compounds **1a–d** as the size of R increases (eq 1)[3] and also accommodates the observed dramatic increase in diastereofacial selectivity that is observed in Lewis acid mediated reactions of chiral aldehydes.[2]



(1)

a: R = Me; b: R = Et; c: R = *i*-Pr; d: R = *t*-Bu.

The trajectory described by a nucleophile when it attacks a carbonyl, first deduced from a consideration of crystal structures of amino ketones, was confirmed theoretically by Bürgi, Dunitz, and co-workers.[4] These calculations, carried out on formaldehyde, showed that approach occurs on a plane perpendicular to the plane of the molecule, at an angle of approximately 107°, now known as the "Bürgi–Dunitz angle". Several research groups[5] have worked to extend the accuracy of these calculations by considering different nucleophiles and by including the counterion in the calculated model.[6] However, except for a brief consideration in the work of Liotta, Burgess, and Eberhardt,[7] there has been no theoretical investigation of nucleophilic attack on unsymmetric carbonyl compounds.

In order to evaluate the possible magnitude of steric effects such as that proposed[2] on nucleophilic trajectories, we have carried out

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(1) Part 39 in the series "Acyclic Stereoselection". For part 38, see: Oare, D. A.; Heathcock, C. H. *Tetrahedron Lett.* **1986**, *27*, 6169.

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(3) In reductions of **1a–d** the **2**:**3** ratios are 2.8:1, 3.2:1, 5.0:1, and 49:1, respectively; Chērest, M.; Felkin, H.; Prudent, N. *Tetrahedron Lett.* **1968**, 2199.

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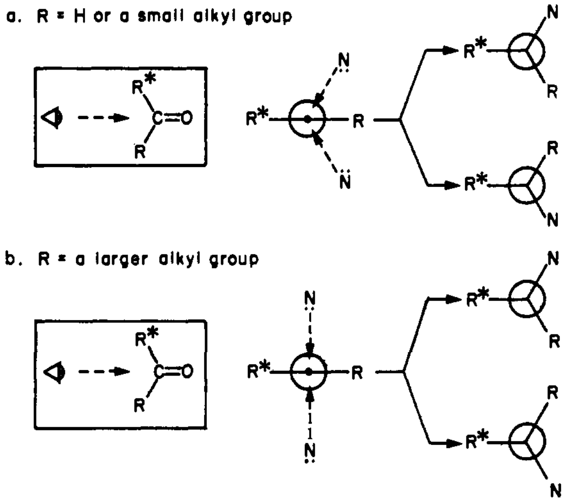
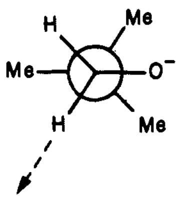


Figure 1. Proposed trajectory of a nucleophile attacking a chiral carbonyl compound.

a series of MNDO calculations[8] using Stewart's MOPAC program.[9] Our calculations model the attack of a hydride on pivalaldehyde. The calculations focus on the deviation of the hydride trajectory from the plane (hereafter called the normal plane) perpendicular to the plane of the carbonyl and containing the C–O bond axis. As the hydride approaches the carbonyl carbon, the aldehyde hydrogen and the *tert*-butyl group will be displaced out of the plane of the carbonyl, so the normal plane is defined as bisecting the H–C_1–O–C_2 dihedral angle. The study was carried out by lengthening one C_1–H bond of conformation **4** over the range 1.15–2.50 Å. The results, compiled in Table I, are conveniently discussed in terms of the Newman projection shown in Figure 2. As the projection clearly shows, the trajectory of the hydride is significantly perturbed from the normal plane away from the *tert*-butyl group. The Bürgi–Dunitz component of the trajectory is essentially the same as is found for attack on formaldehyde.



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A separate series of calculations was performed wherein the hydride was constrained to move on the normal plane. The resulting change in energy associated with this constraint is plotted vs. the hydride–C_1 distance in Figure 3. These results indicate a maximum energy difference of approximately 0.7 kcal/mol, which reflects the maximum influence of the *tert*-butyl group.

The results of our calculations are in qualitative agreement with our hypothesis[2] with regard to the importance of steric effects on nucleophile trajectory as an explanation of the structure–stereoselectivity trends observed by Chèrest, Felkin, and Prudent (eq 1).[3] Clearly, when R is methyl or ethyl the trajectory of an attacking nucleophile should be more on the R side of the normal plane than on the phenylethyl side. When R = isopropyl, the hydride should approach the carbonyl approximately along the normal plane, as phenylethyl is similar in steric bulk to isopropyl. When R = *tert*-butyl, the approach trajectory would be on the phenylethyl side of the normal plane.

Quantitatively, the results are in the correct range as well. The difference in free energy of activation for addition of hydride to the two diastereotopic faces of **1a** is 0.61 kcal/mol, while that for **1c** is 0.95 kcal/mol. The $\Delta\Delta H_f$ of 0.34 kcal/mol is of the same order of magnitude as the calculated $\Delta\Delta H_f°$ values listed in Table I.

Table I. Attack of Hydride on Pivalaldehyde

r, Å	ϕ, deg	α, deg	Bürgi–Dunitz angle, deg	$\Delta\Delta H_f°$, kcal/mol
1.15	1.7	60.6	115.0	
1.20	2.0	61.3	114.5	0.06
1.25	2.3	62.1	113.9	0.06
1.30	2.6	63.0	113.3	0.10
1.35	2.8	63.9	112.8	0.13
1.40	3.1	64.8	112.3	0.15
1.45	3.4	65.8	111.7	0.18
1.50	3.7	66.8	111.1	0.21
1.60	4.4	68.9	110.2	0.28
1.70	5.0	71.2	109.3	0.35
1.80	5.8	73.4	108.6	0.43
1.90	6.6	75.8	107.9	0.50
2.00	7.4	78.0	107.6	0.57
2.10	8.4	80.0	107.6	0.63
2.20	9.4	82.1	107.7	0.68
2.30	10.6	83.7	109.1	0.70
2.40	11.8	85.2	111.0	0.72
2.50	13.2	86.5	113.3	0.72

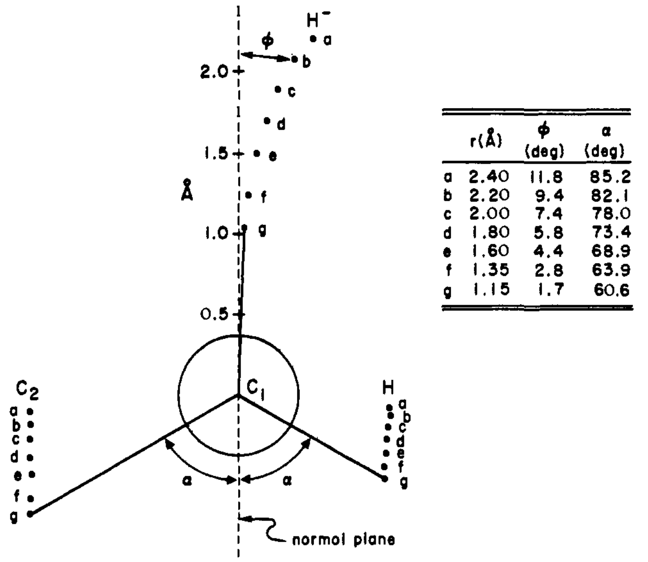

Figure 2. Deviation of the attack trajectory from the normal plane in the reaction of hydride with pivalaldehyde.

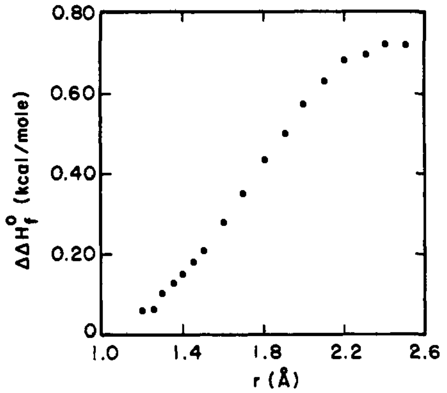

Figure 3. $\Delta\Delta H_f°$ vs. C_1–H distance in attack of hydride on pivalaldehyde.

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