Table II. Hydrogenation of 1-Hexene by Homogeneous Hexane Solution of Cp_2TiCl_2 at Room Temperature

$[Cp_2TiCl_2]$, M × 10^3	No. of molecules/mL of solution × 10^{-18}	Rate of hydrogenation: mL of H_2/min mL of solution	Rate of hydrogenation: mL of H_2/min mL of Ti
0.402	0.242	0.030	74.63
0.722	0.435	0.044	60.94
1.287	0.775	0.049	38.07
1.850	1.114	0.058	31.35
2.530	1.524	0.063	24.90

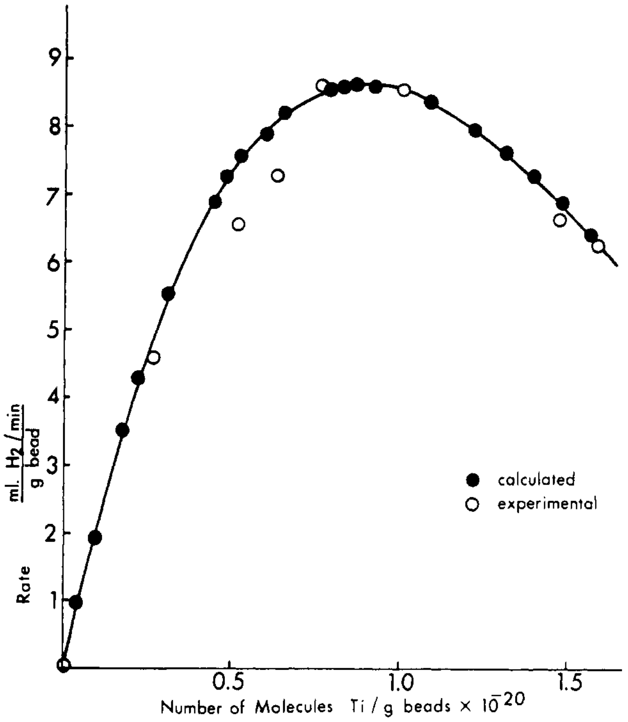

Figure 1. Rate of hydrogenation of 1-hexene as a function of the loading of Ti on the polymer beads.

$$\rho = \frac{\text{number of sites occupied}}{\text{maximum possible sites}} = \frac{(\text{moles loaded})\ (6.023 \times 10^{23}) \times (\text{area of each complex})}{\text{total surface area of polymer}}$$

$$n = 4 \text{ or } 6 \text{ for square sites or circular sites}$$

This equation gives a maximum value for R/k at $\rho = 0.2$ for $n = 4$.[6] In Figure 1, this equation is plotted as a function of R/k vs. ρ. The shape of the curve is reasonable if it is considered that, without any site-site destruction, the rate should increase smoothly with increased loading. However, when sites do interact, the rate is decreased. Site interaction should increase with loading; so the rate-loading relationship should be a sum of two curves with opposite shapes. This result is a curve with a maximum as observed. Figure 1 shows the experimental data plotted on a best-fit calculated curve. The fit is amazingly good considering the sensitivity of the catalyst system to poisoning. From this curve it is easily determined that the maximum rate for hydrogenation is at a loading of 0.14 mmol of Ti/g of polymer. From the calculated ρ at the maximum rate (0.2), the loading of Ti at the maximum rate (0.14 mmol of Ti/g), and the surface area of the polymer used (90 m^2/g),[4] an area for each site can then be calculated. The value for this system is 22 $Å^2$. Although this value is smaller than expected, the difference could be accounted for by recognizing that the dimerization reaction requires a very specific relative orientation of the two adjacent molecules[2] and that the normal surface area measurements may not truly reflect the solution reaction area.

A series of parallel experiments with homogeneous hexane solutions of Cp_2TiCl_2 was carried out. Solutions of varying concentrations were reduced with BuLi and used to catalyze the hydrogenation of 1-hexene. The results (Table II) show an ever lessening increase in hydrogenation rate with increasing catalyst concentration, as one would expect if active catalyst monomer is in equilibrium with an inactive dimer. The data in Table II exhibit no maximum as those in Table I for the polymer-supported catalyst.

This work is most consistent with site isolation on highly cross-linked polystyrene and defines the parameters which can be used to design other experiments requiring site isolation.[6,7]

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(8) Sloan Foundation Fellow.
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Transition State Sensitivity in the Barton Reaction

Sir:

Irradiation of nitrite esters (Barton reaction) provides an elegant way to functionalize an unactivated site intramolecularly.[1] The reaction involves alkoxy radicals that strongly prefer to abstract a hydrogen via a six-membered transition state.[2] We discovered that apollan-11-ol nitrite (**1b**) gives the same oximino alcohol (**3a**) on irradiation as does apollan-*epi*-11-ol nitrite (**1d**).[3] This C-O epimerization in the **1b** → **3a** conversion likely involves a ring-opened radical, **2a** (Scheme I).[3,4] The plane of symmetry in substrates **1b** and **1d** makes C-3

Scheme I

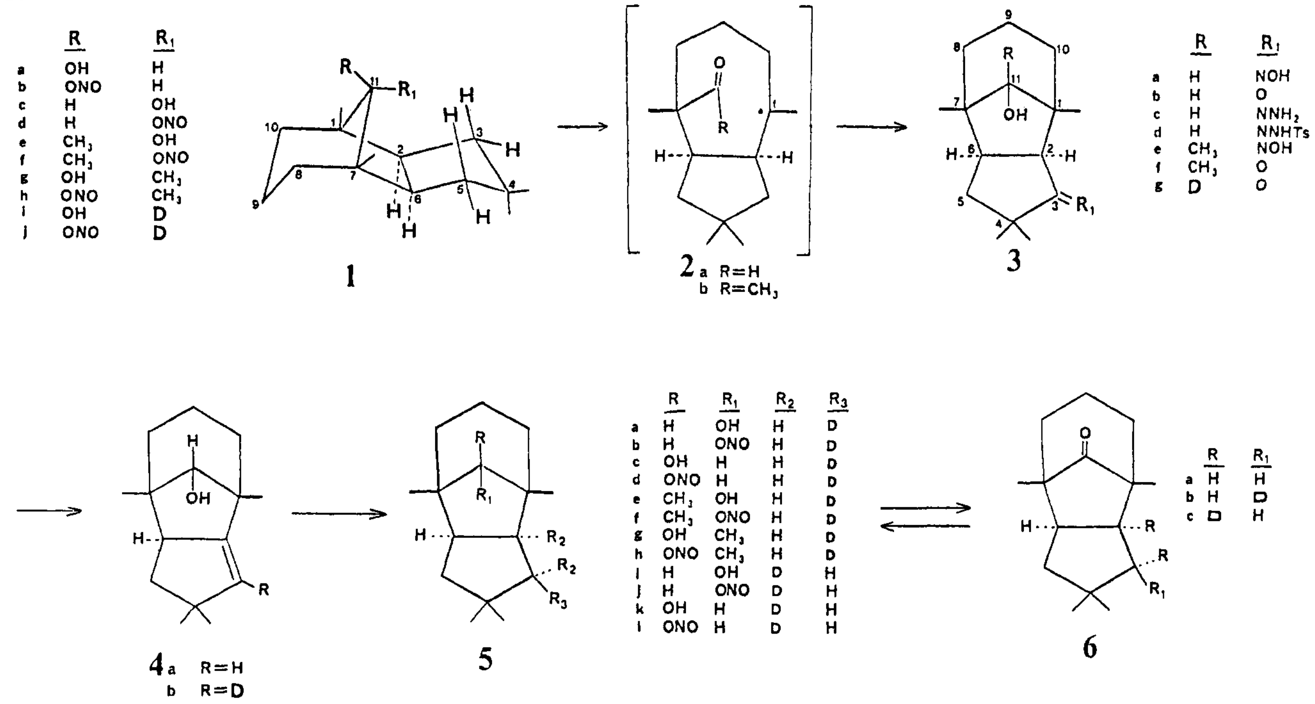

Table I. Primary and Secondary Deuterium Isotope Effects in the Irradiation of Nitrite Esters[a]

Entry	Parent alcohol	Type of alcohol	Isotope effect (k_H/k_D) Primary	Isotope effect (k_H/k_D) Secondary
1	*3β-d*-epi-11-ol (**5a**)	Secondary	4.4 ± 0.2[b]	
2	*3β-d*-11-ol (**5c**)	Secondary	4.2 ± 0.3[b]	
3	*3β-d-tert-epi*-11-ol (**5e**)	Tertiary	1.1 ± 0.1[c]	
4	*3β-d-tert*-11-ol (**5g**)	Tertiary	1.1[d]	
5	2,3α-dideuterio-*epi*-11-ol (**5i**)	Secondary		1.7[e]
6	2,3α-dideuterio-11-ol (**5k**)	Secondary		1.8[f]

[a] In benzene at 80 °C. [b] Average (± average deviation) from eight runs on four different samples whose initial *d* content ranged from 10.4 to 11.9% d_0, 89.6 to 88.1% d_1. [c] Average (± average deviation) from four runs conducted on two different samples whose initial *d* content ranged from 7.1 to 12.3% d_0, 92.9 to 87.7% d_1. [d] Average of two runs. The substrate had 7.1% d_0, 92.9% d_1. [e] Average of two runs. The substrate had 1.2% d_0, 12.3% d_1, 86.5% d_2. [f] Single run due to paucity of material. The substrate had 1.0% d_0, 13.9% d_1, 85.1% d_2.

and C-5 equivalent and can be exploited to probe the transition state of the H-abstraction step, and the epimerization phenomenon simultaneously provides a rare opportunity to compare the behavior of an alkoxy radical generated directly with one that must live long enough to survive an epimerization pathway, irrespective of its mechanistic details.[5] We determined primary and secondary isotope effects (k_H/k_D) in several substrates and wish to report some striking findings. The primary isotope effects were obtained by competitive intramolecular abstraction of the β-oriented D (from C-3) and H (from C-5) in the labeled secondary nitrites **5b** and **5d**, and in tertiary nitrites **5f** and **5h**. Secondary isotope effects were determined with the epimeric nitrites **5j** and **5l**, each of which contains an α-oriented D at the reaction site, C-3, as well as an α-oriented D at C-2. This "extra" D at C-2 results from our method of synthesis. For mass spectral *d* assays the oximino alcohol derived from each irradiation was first hydrolyzed[3] to its corresponding keto alcohol. Therefore in the monolabeled substrates (**5b,d,f,h**), intramoleclar abstraction of D ultimately results in loss of the label, whereas abstraction of H preserves the deuterium. The primary isotope effect (k_H/k_D) is given by (final % d_1)/(original % d_1 − final % d_1). In the bis labeled substrates (**5j,l**), abstraction of β-oriented H from *d*-labeled C-3 ultimately diminishes the d_2 level in the analyzed product, whereas reaction at C-5 does not. Therefore, the secondary isotope effect (k_H/k_D) is given by (final % d_2)/(original % d_2 − final % d_2).

For synthesis of **5b** and **5d**, the known **3b** was convertd to its tosylhydrazone **3d** (mp 195–196.5 °C) by action of hydrazine followed by N-tosylation (TsCl, Et_3N, EtOH, 0 °C) of the hydrazone (mp 155–156 °C).[7] Treatment of **3d** with CH_3Li/TMEDA[6] and workup in H_2O gave **4a**, whose vinyl H appeared as a doublet, δ 5.31 (J = 2.5 Hz) and which gave **1c** on reduction with diimide.[8] When D_2O was used to work up the CH_3Li reaction, we got **4b** (IR 2250, 1630 cm^{-1}; d_0 11.5%, d_1 88.5%).[9] Diimide[8] reduction of **4b** gave **5a** (IR 2150 cm^{-1}), which was oxidized to ketone **6b**.[10] Reduction of **6b** with Na/*i*-PrOH gave **5c** (2150 cm^{-1}), which is the 3β-deuterio analogue of known apollanol, **1a**.[3]

The labeled tertiary alcohols **5e** and **5g** were obtained by addition of CH_3Li to the *d*-ketone **6b** followed by preparative GLC separation of the 60:40 mixture of **5e** and **5g**. Stereochemical assignments in **5e** and **5g** follow from the chemistry of the unlabeled analogues **1e** (liquid) and **1g** (mp 35-36 °C). Thus irradiation of their corresponding nitrites (**1f** and **1h**) and hydrolysis of the derived oximino alcohol (**3e**) gave the same, single keto alcohol **3f** (mp 102–103 °C), which must necessarily have the OH syn to the carbonyl (i.e., epi configuration). Wolff-Kishner reduction of **3f** produced the liquid tertiary alcohol **1e**. This **1h** → **3f** reaction is the first example of C–O epimerization of a *tertiary* alcohol in a Barton reaction, and likely involves radical **2b** as in intermediate.

The dideuterated alcohol **5i** (2170 cm^{-1}) was obtained from **4a** by reduction with dideuteriodiimide.[8] Jones oxidation[10] gave ketone **6c** (2180 cm^{-1}; typical d_0 1.5%, d_1 13.5%, d_2 85%), which was reduced with Na/*i*-PrOH to **5k** (2180 cm^{-1}).

Our *d*-alcohols were converted to their nitrites (**5b,d,f,h,j,l**) and irradiated in benzene as reported,[3] and the derived oximino alcohols were hydrolyzed to ketoalcohols for mass spectral analysis. Table I summarizes the k_H/k_D results.

The first important conclusion is that epimers exhibit the same isotope effect (cf. entries 1 vs. 2; 3 vs. 4; 5 vs. 6). Therefore the alkoxy radicals from both epimers behave the same in the transition state for H-abstraction even though one of these radicals cannot be in an electronic or vibrational "excited" state because it has to survive an epimerization pathway before it can abstract.[5] Because an "excited" (i.e., high energy) species is expected to show less isotopic discrimination than a ground-state species, this is the first direct evidence that ground state rather than excited alkoxy radicals perform the H-abstraction, even when these radicals are generated photically.[11]

The second striking finding is that, whereas the primary isotope effect of 4.3 (at 80 °C) for the secondary alcohols (entries 1 and 2)[12] indicates appreciable C–H weakening[13] in the cyclic transition state, the corresponding tertiary alcohols (entries 3 and 4) show almost no primary isotope effect (viz., ~1.1).[14] Because of the locked skeleton in these tricyclic substrates, the C–O radical from the secondary and tertiary alcohols cannot differ much in spatial location, and so we conclude that even *slight* changes in molecular geometry can markedly alter the bonding situation in the transition state. In view of this sensitivity, the known[2,15] remarkable regioselectivity of the Barton reaction (even for two competing six-membered transition states) is more understandable.

The third notable finding (entries 5 and 6) is the size (~1.7) of the secondary isotope effect, which appears to be one of the highest observed.[16] The reasons for its magnitude are obscure especially since we don't know if the 2α-D exerts any effect. (This 2α bond should not interact strongly with C-3 via hyperconjugation if the transition state is truly radical-like and not ionic-like.[17]) Among other things, we are considering the possibility that slight differences in average (nonharmonic) vibrational amplitudes[18] of C–D and C–H destroy the apparent skeletal symmetry of the labeled substrates. For intramolecular competition, any such slight distortion could, in effect, enhance (or diminish) an inherent isotope effect,[16] when a transition state is very sensitive to geometry.

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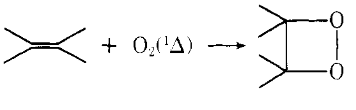
Intermediates in the Chemiluminescent Reaction of Singlet Oxygen with Ethylene. Ab Initio Studies

Sir:

The excited singlet state of dioxygen molecule, $^1O_2$, is thought to play an important role in such biologically important phenomena as "photodynamic action" (photosensitized oxidation),[1] photocarcinogenicity,[2] photochemical smog formation,[3] and bioluminescent processes.[4] However, despite numerous experimental studies[5,6] of the chemistry of $^1O_2$, there is yet a great deal of uncertainty concerning the mechanism involved in the reactions of $^1O_2$ and in the chemiluminescence[7] that often results. In this paper we will use the results of ab initio studies (large basis including polarization functions; generalized valence bond[8] with extensive configuration interaction) to examine the processes 1, 2, and 3.



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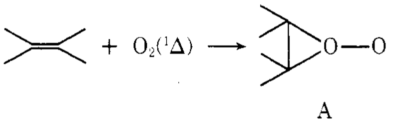

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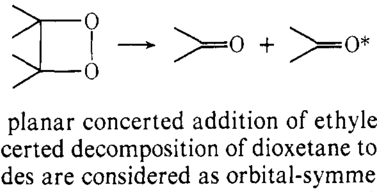

(3)

Both the planar concerted addition of ethylene to $O_2(^1\Delta)$ and the concerted decomposition of dioxetane to ground-state formaldehydes are considered as orbital-symmetry-forbidden processes.[9] Three alternative mechanisms have been proposed for the addition reaction: (1) a nonplanar $[2_s + 2_a]$ concerted addition,[9,10] (2) a stepwise addition involving an acyclic biradical or zwitterionic (CCOO) intermediate,[11] and (3) a stepwise addition through a peroxirane (B) intermediate.[9,11,12]