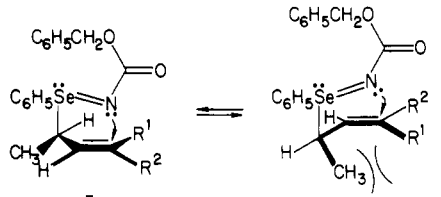
We have previously suggested[4a] that the NCS/carbamate promoted rearrangement of allylic selenides to N-protected allylic amines (i.e., **2** → **3**) proceeds via [2,3]-sigmatropic rearrangement of an intermediate selenimide. This conclusion was based upon both the olefin stereochemistry and allylic transposition observed in the isolated products. The results described herein further support the involvement of a [2,3]-sigmatropic rearrangement, since, qualitatively, the conversion of (*R*)-(*Z*)-**2** to (*R*)-(*E*)-**3** demonstrates that the rearrangement reaction is suprafacial with respect to the allylic component. This is consistent with rearrangement occurring via transition state **5** (R_1 = alkyl; R_2 = H), rather than it rotamer **6** (R_1 = alkyl; R_2 = H), in order to minimize allylic $A^{1,3}$ strain during C–N bond formation.[5] The additional observation that the *E* isomer of racemic **2** (R = H) rearranges in ca. 50% yield to racemic **3** (R = H) of greater than 97% E configuration[16] allows the quantitative assessment of the enantiomeric excess data. This observation implies that the *E* isomer of (*R*)-**2**, a contaminant in (*R*)-(*Z*)-**2**, is responsible for the production of the undesired (*S*)-(*E*)-**3**, and ultimately the protected L-α-amino acids.[17] After correction for the presence of ca. 3% of the enantiomer of (*R*)-**1** in the starting aldehyde and the implied formation of the enantiomer of **3** from (*E*)-**2**, the overall enantiomeric excess values of 78–84% found for the protected amino acid products are consistent with the rearrangement step proceeding with high stereogenic[2] fidelity and as represented by transition state **5**.[18]



5 **6**

In addition to providing a nonresolutive, general synthesis of N-protected, D-α-amino acids from an inexpensive optically active precursor, these results clearly establish the selenide to amine rearrangement reaction as a stereocontrolled process which has appreciable potential in the synthesis of stereochemically complex amines.[19]

Registry No. (*R*)-**1**, 94292-14-5; **2** (R = H), 94202-76-3; **2** (R = C_6H_5), 94234-87-4; **2** (R = $CH(CH_3)_2$), 94202-77-4; **2** (R = $(CH_2)_2CH_3$), 94202-78-5; **3** (R = H), 94202-79-6; **3** (R = C_6H_5), 94202-80-9; **3** (R = $CH(CH_3)_2$), 94202-81-0; **3** (R = $(CH_2)_2CH_3$), 94202-82-1; **4** (R = H), 26607-51-2; **4** (R = C_6H_5), 2448-45-5; **4** (R = $CH(CH_3)_2$), 28862-79-5; **4** (R = $(CH_2)_2CH_3$), 15027-14-2; H_3C-$CH{=}P(C_6H_5)_3$, 1754-88-7; $C_6H_5CH_2CH{=}P(C_6H_5)_3$, 53213-08-4; $(CH_3)_2CHCH_2CH{=}P(C_6H_5)_3$, 39110-24-2; $CH_3(CH_2)_2CH_2CH{=}P(C_6H_5)_3$, 29541-98-8; $C_6H_5CH_2OC(O)NH_2$, 621-84-1; ethyl (*S*)-lactate, 687-47-8; sodium phenyl selenide, 23974-72-3; ethyl (*R*)-2-(phenylselenenyl)propionate, 94202-83-2; CH_3SO_2Cl, 124-63-0.

(14) Enantiomeric excess determined by HPLC analysis of the dansyl derivatives (1. 20% $Pd(OH)_2/C$, cyclohexene, EtOH; 2. dansyl chloride, H_2O, THF, Et_3N). See: Lam, S.; Chow, F.; Karmen, A. *J. Chromatogr.* **1980**, *199*, 295). We find UV detection at 335 nm to be a satisfactory alternative to fluorescence detection.

(15) Substitution of *tert*-butyl carbamate for benzyl carbamate permits the preparation of *t*-BOC-protected D-α-amino acids. Thus we have prepared *t*-BOC-D-norleucine in yield and ee comparable to CBZ-D-norleucine.

(16) A comparison sample of (*Z*)-**3** was prepared from ethylidenetriphenylphosphorane and *N*-Cbz-alanal.[13] The conversion of racemic (*E*)-**2** to nearly exclusively racemic (*E*)-**3** was anticipated on the basis of a previously reported allylic *N*-tosylselenimide rearrangement.[4c]

(17) Rigorous demonstration that (*R*)-(*E*)-**2** rearranges to (*S*)-(*E*)-**3** is currently precluded by the unavailability of the requisite optically active allylic selenides but will be pursued in due course.

(18) We are currently unable to comment on the role played by chirality at selenium during this rearrangement. Illustrations **5** and **6** are not meant to accurately describe stereochemistry with respect to the selenimide functionality.

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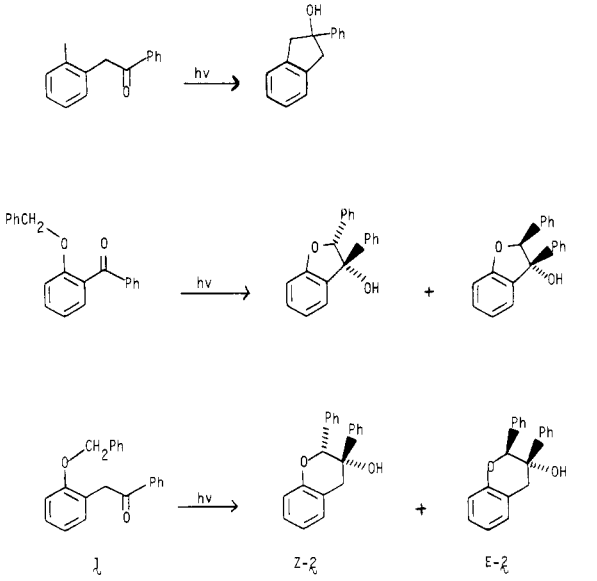
Photocyclization of α-[*o*-(Benzyloxy)phenyl]acetophenone: Triplet-State ε-Hydrogen Abstraction

Summary: The first example of efficient photocyclization due to ε-hydrogen abstraction by a triplet ketone is reported.

Sir: We recently reported the highly efficient photocyclization of α-(*o*-tolyl)acetophenones to 2-phenyl-2-indanols.[1] This reaction proceeds via triplet-state δ-hydrogen abstraction. *o*-Alkoxyphenyl ketones are also well known to photocyclize via triplet-state δ-hydrogen abstraction.[2,3] We decided to see whether a heretofore unknown ε-hydrogen abstraction might be possible in the title compound **1**, which combines the structural features which promote the two efficient δ-hydrogen abstractions.

Preparation of **1** from commercial *o*-hydroxybenzaldehyde was straightforward: benzylation of the phenol, reduction of the aldehyde, conversion of alcohol to chloride, displacement of Cl by lithium 2-phenyl-1,3-dithiolane, and mercuric-catalyzed hydrolysis. A cyclohexane solution of **1** (1.2 g in 200 mL) was purged with nitrogen and irradi-



1 **Z-2** **E-2**

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(2) (a) Pappas, S. P.; Pappas, B. B.; Blackwell, J. E. *J. Org. Chem.* **1967**, *32*, 3066. (b) Lappin, G. R.; Zannucci, J. S. *Ibid.* **1974**, *36*, 1808.
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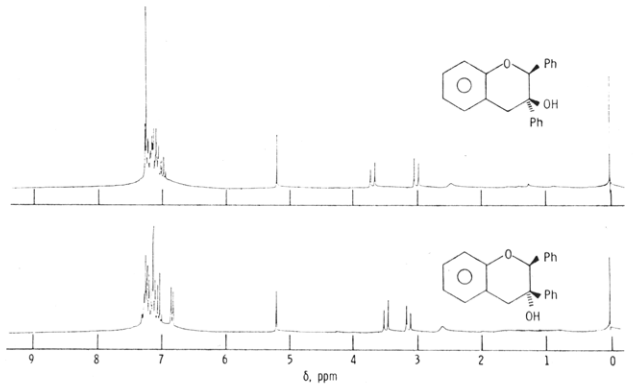


Figure 1. ^1H NMR spectra (250-MHz) of the two diphenylbenzodihydropyranol photoproducts in $CDCl_3$.

ated for 24 h with a Pyrex-filtered 450-W mercury arc. HPLC and NMR analysis of the crude photolysate indicated a ≥80% yield of two isomeric products in a ratio of 1.6/1. Flash chromatography[4] on silica gel with 9:1 hexane/ethyl acetate eluent isolated the two isomers which were identified as the isomeric 2,3-diphenyl-3-hydroxy-3,4-dihydrobenzopyrans **2** by their ^1H NMR spectra ($CDCl_3$) which are shown in Figure 1. The broad singlets at 2.5–2.7 ppm are hydroxyls. The major isomer is assumed to be *Z* (with the two phenyl rings trans), in accord with all other ketone-derived biradical cyclizations.[5,6] This assignment is supported by the doublet at 6.8 ppm assigned to (*E*)-**2**, which is due to one conformer having a 3-phenyl axial, such that its ortho protons are in the shielding cone of the benzopyran benzene ring.

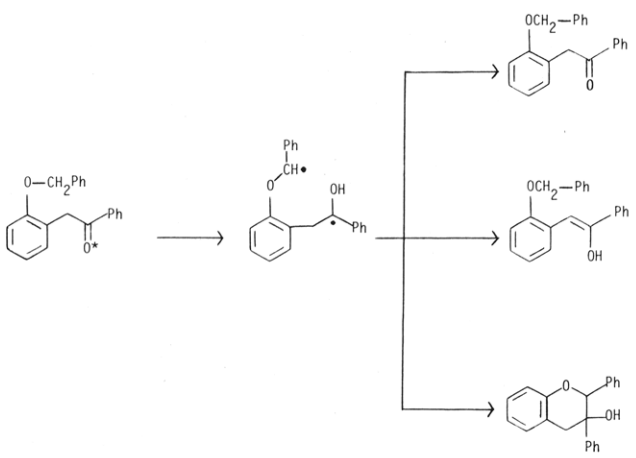
The quantum yield for the photocyclization is only 0.045 in benzene and is increased only slightly to 0.05 by the presence of 2 M pyridine. The reaction is readily quenched with conjugated dienes, $k_q\tau = 183 \pm 9$ M^{-1} in benzene. With $k_q = 6 \times 10^9$ M^{-1} s^{-1},[7] the rate of triplet decay is 3×10^7 s^{-1}. This value is much faster than radiationless decay of the triplet, so some subsequent process must be responsible for low quantum yields.

We assume that the cyclization arises by triplet state ϵ-hydrogen abstraction to generate a 1,6-biradical intermediate. The actual rate of hydrogen abstraction is comparable to that for δ-hydrogen abstraction by triplet *o*-(benzyloxy)benzophenone.[3] The insignificant rate effect caused by the extra methylene group in **1** is not surprising in light of the very large rate constants for δ-hydrogen abstraction found in the α-tolyl ketones, which have restricted conformational flexibility.[1]

The presumed 1,6-biradical intermediate has three major reactions available to it (Scheme I). Two of these paths involve internal disproportionation to the starting ketone or its enol. We have recently shown that disproportionation to enol via a 1,4-hydrogen transfer is the major reaction of several 1,5-biradicals.[6] Such a reaction involves a 1,5-H transfer in this 1,6-biradical and therefore might well dominate both cyclization and 1,7-hydrogen transfer back to ketone. We suggest that this competition causes the low cyclization quantum yield.

These results establish that ϵ-hydrogen abstraction, like δ, can occur cleanly in ketones with suitable conformational restraints. The reaction leads in this case to a high-yield

Scheme I



preparation of benzopyrans. We are now exploring the scope of this new photoreaction.

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Registry No. **1**, 94203-48-2; (*Z*)-**2**, 94203-50-6; (*E*)-**2**, 94203-49-3.

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Enantioselective Synthesis of Swainsonine, a Trihydroxylated Indolizidine Alkaloid

Summary: A total synthesis of (−)-swainsonine in 21 steps and 6.6% overall yield starting from *trans*-1,4-dichloro-2-butene and *N*-benzyl-*p*-toluenesulfonamide is described. The synthesis employs the methodology of the Masamune/Sharpless approach to polyhydroxylated natural products.

Sir: The indolizidine alkaloid swainsonine[1] (**1**) is known to be an effective inhibitor of both lysosomal α-mannosidase[2] and mannosidase II.[3] Lysosomal α-mannosidase is involved in the cellular degradation of polysaccharides, while mannosidase II is a key enzyme in the processing of asparagine-linked glycoproteins.[4] The use of swainsonine as a biochemical tool for the study of these systems has been limited by its lack of availability. In the past year, three syntheses of swainsonine have appeared, each starting from a glucose or mannose derivative.[5]

Swainsonine is believed to be a substrate-site directed inhibitor of α-mannosidase.[2] Part of the rationale behind

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