

now, we note that kinetic trans oxaphosphetane selectivity is a logical consequence of an asynchronous cycloaddition with a relatively advanced, product-like transition state because the trans oxaphosphetanes are more stable than the cis isomers in all known examples of isomer interconversion.⁶ Since 4 reacts with a kinetic preference for (*E*)-alkenes, equilibrium arguments for related Wittig reactions of stabilized ylides with aliphatic aldehydes are neither necessary nor justified.

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Registry No. 4, 110223-71-7; 5, 110223-68-2; 8-OTf⁻, 110223-70-6; 8-d, 110223-72-8; cyclohexanecarboxaldehyde, 2043-61-0.

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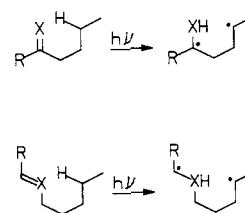
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Photochemical 1,5-Hydrogen Transfer of 1,2-Disubstituted Acyclic Alkenes. A Novel Entry to 1,6-Diradicals

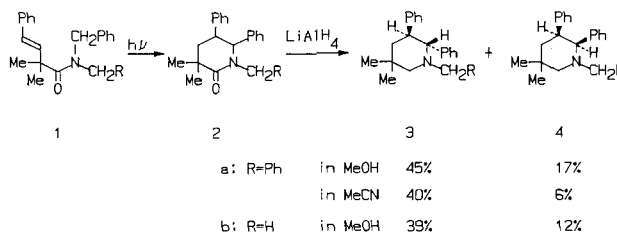
Summary: Photolysis of β,γ -unsaturated amides **1a** and **1b** gives cyclization products **2a** and **2b** via 1,6-diradical intermediates formed by 1,5-hydrogen transfer.

Sir: Photochemical 1,5-hydrogen transfer of carbonyl compounds (Norrish type II reaction),¹ thioketones,² and 1,1-disubstituted alkenes³ is one of the most extensively studied photoreactions. In these reactions, the hydrogen transfer via six-membered cyclic transition states gives 1,4-diradicals (Scheme I) which undergo either elimination or cyclization to give four-membered cyclic compounds. It is well-known that 1,6-hydrogen transfer is sterically less favorable than 1,5-hydrogen transfer.^{4,5} 1,7-Hydrogen transfer which gives 1,6-diradicals via eight-membered cyclic transition states (ϵ -hydrogen abstraction) is extremely rare because of highly unfavorable conformational factors.^{2,6,7,8} Photochemical 1,5-hydrogen transfer of 1,2-disubstituted acyclic alkenes (or imines) via sterically favorable six-membered transition states could give 1,6-diradicals (Scheme I). However, such reactions are hitherto unknown presumably because of the presence of rapid

Scheme I



Scheme II



competitive processes in the excited states, e.g., *E-Z* isomerization. We report here the first example of 1,5-hydrogen transfer of acyclic 1,2-disubstituted alkenes which produces 1,6-diradicals.⁹

When *N,N*-dibenzyl-2,2-dimethyl-4-phenylbut-3-enamide (**1a**) in methanol is irradiated with a low-pressure mercury lamp,¹⁰ 3,3-dimethyl-5,6-diphenyl-1-benzylpiperidin-2-one (**2a**) was obtained. The cyclization product was a mixture of two stereoisomers which were not completely separated. The separation was achieved after conversion into the corresponding piperidines **3a** and **4a** by reduction with lithium aluminum hydride (Scheme II). Photolysis of **1a** in acetonitrile gave a similar result. The structures of **3a** and **4a** were confirmed by elemental analyses and spectral data.¹¹ The stereochemistry of **3a** and **4a** was assigned as shown in Scheme II on the basis of the coupling constant between the vicinal protons on C-2 and C-3 in the NMR spectrum of **4a** (6 Hz). The stereoselectivity in the photocyclization is explainable in terms of the stabilities of the products: the major isomer is presumed to be more stable than the minor one because both of the phenyl groups are equatorial.

Photolysis of an *N*-benzyl-*N*-methyl amide (**1b**) also gave the corresponding cyclization products. In this reaction, no methyl-hydrogen-abstraction products were detected. Meanwhile, an *N,N*-diethyl amide (**1c**) did not afford cyclization products on irradiation but underwent only *E-Z* isomerization.

The formation of **2** is quite reasonably explained in terms of 1,5-hydrogen transfer followed by cyclization of the resulting 1,6-diradical **5**. The regiospecific benzyl-hydrogen-abstraction in the photolysis of **1b** as well as the

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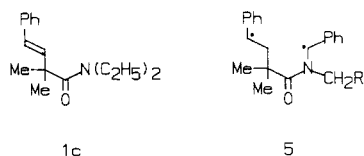
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(10) The unsaturated amide (300 mg) in methanol (60 mL) was irradiated with a low-pressure mercury lamp (Rayonet Photochemical Reactor RPR 2537 A, the Southern New England Ultraviolet Co) for 4.5 h.

(11) **3a**: mp 112–113 °C; ¹H NMR (CDCl₃) δ 0.88 (s, 3 H, Me), 1.26 (s, 3 H, Me), 1.52–1.72 (m, 2 H, CH₂), 1.92 and 2.64 (AB q, 2 H, J = 11 Hz, NCH₂), 2.81 and 3.77 (AB q, 2 H, J = 14 Hz, benzylic), 2.96–3.24 (m, 2 H, 2-H and 3-H), 6.6–7.8 (m, 15 H, Ph); ¹³C NMR (CDCl₃) δ 24.4 (q), 29.7 (q), 30.6 (s), 46.1 (t), 48.6 (d), 59.3 (t), 64.3 (t), 74.7 (d), 125.8–128.0, 140.0 (s), 142.8 (s), 143.5 (s); mass spectrum (EI) *m/z* 355 (M⁺). **4a**: bp 150–160 °C (0.1 Torr (bath temperature)); ¹H NMR (CDCl₃) δ 1.09 (s, 3 H, Me), 1.15 (s, 3 H, Me), 1.43 (dd, 1 H, J = 3 Hz and J = 13 Hz, 4-H), 2.19 (t, 1 H, J = 13 Hz, 4-H), 2.33 and 2.72 (AB q, 2 H, J = 11 Hz, NCH₂), 3.34 and 3.49 (AB q, 2 H, J = 14 Hz, benzylic), 3.4–3.7 (m, 1 H, 3-H), 4.00 (d, 1 H, J = 6 Hz, 2-H), 6.7–7.4 (m, 15 H, Ph); ¹³C NMR (CDCl₃) δ 26.4 (q), 30.2 (q), 31.4 (s), 37.2 (t), 42.7 (d), 58.1 (t), 59.6 (t), 69.3 (d), 125.7–130.1, 139.7 (s), 139.9 (s), 142.7 (s); mass spectrum (EI) *m/z* 355 (M⁺). The compounds **3a** and **4a** gave satisfactory analytical data (0.25%).



nonreactivity of the methylene hydrogens of **1c** toward abstraction indicates that stabilization of the 1,6-diradical **5** is necessary for the 1,5-hydrogen transfer.

Much attention has recently been given to investigations on diradicals.¹² 1,6-Diradicals have been generated by 1,7-hydrogen transfer (vide supra) or Norrish type I reaction (α -cleavage) of cyclohexanones.¹³ The results of the present reactions indicate that 1,5-hydrogen transfer of 1,2-disubstituted alkenes becomes possible when the hydrogens are strongly activated by substituents. This kind of photoreaction provides a novel entry to the 1,6-diradicals.

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Crystal Engineering a Solid-State Diels-Alder Reaction

Summary: [3,4-(Methylenedioxy)phenyl]propionic acid was predicted to and does in fact crystallize with a short axis of 4 Å and with a packing such that diene and dienophile components in adjacent molecules may participate in an intermolecular solid-state Diels-Alder reaction.

Sir: Crystal engineering is concerned with the predictive design of topochemical processes, by understanding the nature of weak yet directionally specific nonbonded forces.¹ Here, we describe such a deliberately "engineered" intermolecular solid-state Diels-Alder reaction which seems quite general and may offer considerable scope for a more systematic chemistry of molecular solids.

The strategy involved identification of a substance which may act as either diene or dienophile and further crystallize in a structure which permits a topochemical 4 + 2 conversion. Accordingly, substituted phenylpropionic acids were considered; not only are they used in self-Diels-Alder reactions in lignan synthesis^{2,3} but the crystallography of the structurally related *trans*-cinnamic acids has been extensively investigated.^{4,5}

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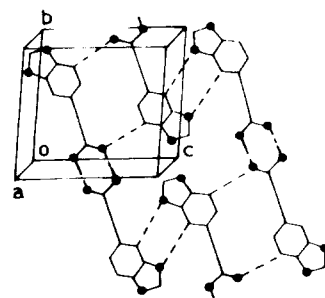


Figure 1. View of the crystal structure of [3,4-(methylenedioxy)phenyl]propionic acid (**2**) down the 4-Å short axis. The molecular sheets lie parallel to (111). O-H...O and C-H...O bonds are indicated.

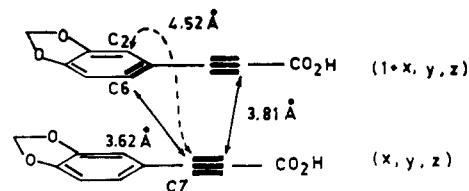
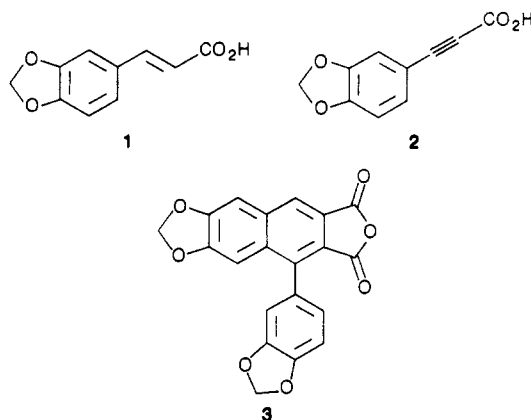


Figure 2. Schematic view of a topochemical Diels-Alder reaction for acid **2**.

The methylenedioxy substituent may "steer" the crystal structure of a planar aromatic to the 4-Å short axis structure (β structure) because of in-plane C-H...O interactions which stabilize the formation of two-dimensional molecular motifs.^{5,6} In 3,4-(methylenedioxy)cinnamic acid (**1**), for instance, these motifs are planar sheets, stacking of which leads to the 4-Å axis. Additionally, other factors



being constant, a planar aromatic having a higher C/H stoichiometric ratio prefers the β and related structures with overlapping, stacked molecules.⁷ So, 1,4-diethylnaphthalene, C₁₄H₈, adopts the β structure,⁸ while naphthalene, C₁₀H₈, with a lower C/H ratio, does not. Analogously, one may extrapolate from the β structure of **1**, C₁₀H₈O₄, that of [3,4-(methylenedioxy)phenyl]propionic acid (**2**), C₁₀H₈O₄. Both **1** and **2** are planar molecules with similar volumes, shapes, and functionalities. The smaller number of hydrogen atoms in **2** was expected, in fact, to enhance the tendency for β structure adoption.

This prediction was confirmed in its crystal structure analysis.⁹ Figure 1 shows that molecules of **2** form a

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