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Novel Photocatalytic Product from *m*-Nitrocinnamic Acid and Alcohol Mediated by TiO_2

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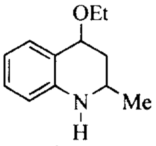
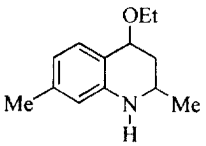
Abstract: New heterocycles **6** having a skeleton of 7-membered lactone and a 1,2,3,4-tetrahydroquinoline were obtained from TiO_2 suspended alcoholic solution of *trans* *m*-nitrocinnamic acid **4** by uv (350 nm) irradiation. Highly functionalized products **6** are believed to be formed through 4-alkoxy-1,2,3,4-tetrahydroquinolines **5**. © 1999 Elsevier Science Ltd. All rights reserved.

Titanium dioxide (TiO_2), a photocatalyst, has been utilized not only in diverse fundamental chemical redox reactions[1] but also in practical applications such as environmental purification.[2] Despite the innumerable examples of photocatalytic degradations[3] and transformations[4] mediated by TiO_2, relatively limited reports on inducing intermolecular bondings have appeared. N-Alkylation of various amine[5] and synthesis of 2-alkylbenzimidazole from *o*-dinitrobenzene in TiO_2 suspended alcohols[6] are among the examples. Recently, we found out a one-pot synthesis of 4-ethoxy-2-methyl-1,2,3,4-tetrahydroquinolines **1-3** by uv irradiation of ethanolic solution of nitroarene in the presence of TiO_2.[7] At that time, however, reactions were carried out only in ethanol and stereostructures of the products **1-3** were not determined.



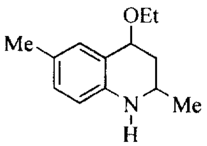
1

(from nitrobenzene)



2

(from *m*-nitrobenzene)



3

(from *p*-nitrobenzene)

Herein we report unexpected heterocycle **6** having an unusual skeleton of 7-membered lactone and a tetrahydroquinoline produced from alcoholic solutions of *m*-nitrocinnamic acid **4** mediated by TiO_2 under irradiation of uv light. The results are listed in Table 1. When ethanol was used, **6a** was isolated in 30%. Similar reactions in *n*-propanol and *n*-butanol were worked up to get inseparable

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stereoisomers in 14% and 15% respectively.[8]

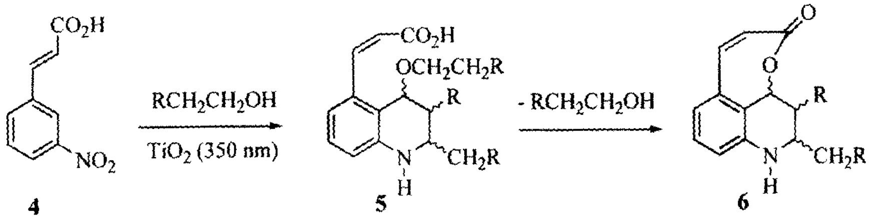
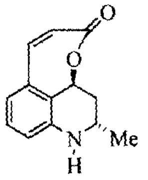
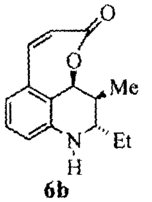
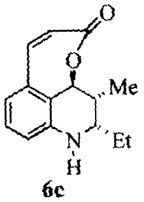
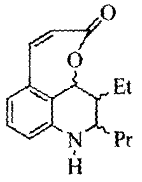


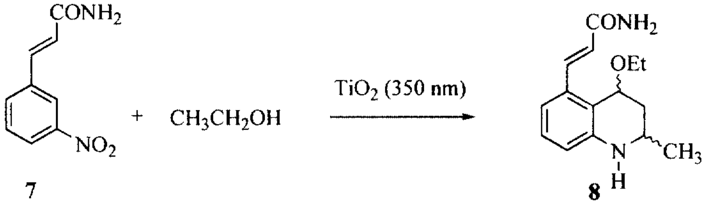
Table 1. Photocatalytic Products Obtained from **4** and Alcohol Using TiO_2

Alcohol	Isolated Products (yield %)
EtOH	 **6a** (30%)[a]
n-PrOH	 **6b** +  **6c** (14%)[b]
n-BuOH	 **6d** (15%)[c]

[a]Quantitative yield determined by GC was 37%. [b]Quantitative yield by GC was 19%. ^{1}H NMR spectrum showed that the ratio of **6b** to **6c** was 2.5: 1.0. [c]Mixture of three inseparable mixtures with a ratio of 5.3:1.0:1.0 based on ^{1}H NMR spectrum. Quantitative yield by GC was 19%.

Stereochemistry of **6a** was unambiguously assigned by the splitting patterns of the protons at C-1, C-2 and C-10a. *i.e.* axial proton at C-1 showed ddd splitting pattern by geminal (J=14.4Hz), axial-axial (J=12.2Hz), and axial-equatorial (J=4.8Hz) couplings. On the other hand, equatorial proton at C-1 showed dt splitting pattern by geminal (J=14.4Hz), axial-equatorial (J=2.1Hz), equatorial-equatorial (J=1.2Hz) couplings.[9]

Product **6** is believed to be formed through 1,2,3,4-tetrahydroquinoline **5** which can undergo intramolecular cyclization by displacing alkoxy group. Intervention of **5** was confirmed indirectly using *m*-nitrocinnamide **7** which produced only **8** without making intramolecular cyclization.



Noteworthy in the formation of **6** is the mode of cyclization. Substrates **4** and **7** gave products by cyclizing at a more sterically hindered carbon between two substituents. A plausible reason for this would be due to hydrogen bonding between the proton in the carboxyl/amide group and oxygen in alkyl vinyl ether which has been proposed as one of the intermediates in these reactions.[7]

Other semiconductor photocatalysts such as Pt-TiO$_2$ (physical mixture of 3wt% Pt), CdS, and CdS.ZnS[10] were also examined in order to compare the surface effects on the course of the synthesis of **6**. Pt-TiO$_2$ was more efficient than bare TiO$_2$ (Degussa P-25). *i.e.* yield of **6a** was increased to 40% using Pt-TiO$_2$, but the other chalcogenide semiconductors were not effective to make any cyclization product. The nitro groups are likely to be more tightly adsorbed onto the surface of the oxide semiconductor rather than on the chalcogenides.

In overall, we have demonstrated examples in which redox couples self assemble in an unique way to afford new heterocycles **6** in moderate yields. These photocatalytic reactions might provide a useful synthetic methodology, difficult to reach by conventional methods.

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8. Reactions conditions were not optimized. Other unknown products were also formed in addition to **6b,c** and **6d**.
9. **6a**: ^{1}H NMR (300 MHz, chloroform-d) δ 1.30 (d, *J*=6.3, 3H, CH_3), 1.69-1.78 (ddd, *J*=14.4, *J*=12.2, *J*=4.8, 1H, axial H at C-1), 2.34-2.39 (d of apparent t, *J*=14.3, *J*=1.7, 1H, equatorial H at C-1), 3.43-3.53 (dqd, *J*=12.2, *J*=6.3, *J*=2.1, 1H, H at C-2), 4.13 (br, 1H, NH), 5.16-5.18 (dd, *J*=4.8, *J*=1.2, 1H, H at C-10a), 6.32 (d, *J*=12.0, 1H, vinyl-H at C-8), 6.69 (d, *J*=8.3, 1H, Ph-H at C-4), 6.74 (d, *J*=7.4, 1H, Ph-H at C-6), 7.14 (d, *J*=12.0, 1H, vinyl-H at C-7), 7.19 (apparent t, *J*=7.80, 1H, Ph-H at C-5). ^{13}C NMR (75.4 MHz, chloroform-d) δ 21.3 (CH_3 at C-2), 36.9 (C-1), 42.6 (C-2), 69.8 (C-10a), 116.5 (C-4), 117.4 (C-6b), 118.6 (C-6), 122.6 (C-8), 129.9 (C-5), 136.2 (C-6a), 140.7 (C-7), 145.4 (C-6c), 168.0 (C-9). GC/MS; 215 (M^+), 200, 187, 172, 156, 143, 128, 102, 89, 77. Anal. Calcd. for $C_{13}H_{13}NO_2$: C, 72.53; H, 6.09; N, 6.51. Found: C, 72.86; H, 5.93; N, 6.51.
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