Pergamon

Tetrahedron Letters 39 (1998) 2791–2792

TETRAHEDRON
LETTERS

A Novel, Stereoselective Photo-Ritter Reaction of 1,1-Diphenyl-1,6-heptadiene via Photoinduced Electron Transfer Reaction

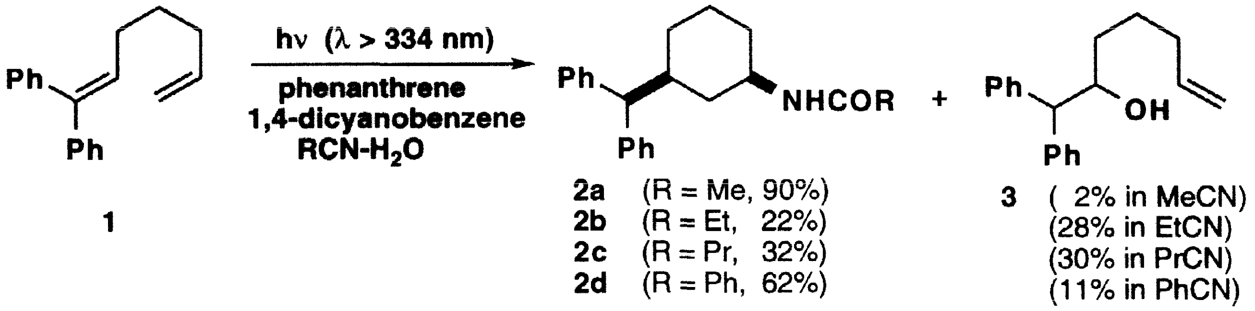
Hideki Ishii, Takashi Hirano,* Shojiro Maki, Haruki Niwa,* and Mamoru Ohashi†

Department of Applied Physics and Chemistry, The University of Electro-Communications, Chofu, Tokyo 182, Japan
†Department of Materials Science, Kanagawa University, Hiratsuka, Kanagawa 259-12, Japan

Received 22 December 1997; revised 12 February 1998; accepted 13 February 1998

Abstract: Irradiation of a wet acetonitrile nitrile solution of 1,1-diphenyl-1,6-heptadiene in the presence of 1,4-dicyanobenzene and phenanthrene provided *cis*-1-acetamido-3-(diphenylmethyl)cyclohexane in high yields with high stereoselectivity. Several examples leading to *cis*-1-acylamino-3-(diphenylmethyl)cyclohexanes were also described.

Photosensitized electron transfer reaction offers versatile method for generating radical cation species from electron-rich olefins and aromatic compounds.[1] We are currently investigating the synthetic application of radical cations generated from 1,1-diphenylethylene-based substrates by using the redox photosensitized electron transfer reaction.[1b] Herein we wish to disclose the highly stereoselctive Ritter reaction with a 6-membered ring formation induced by phenanthrene-sensitized photo-electron transfer reaction (Scheme **1**).[2]



1

2a (R = Me, 90%)
2b (R = Et, 22%)
2c (R = Pr, 32%)
2d (R = Ph, 62%)

3 (2% in MeCN)
(28% in EtCN)
(30% in PrCN)
(11% in PhCN)

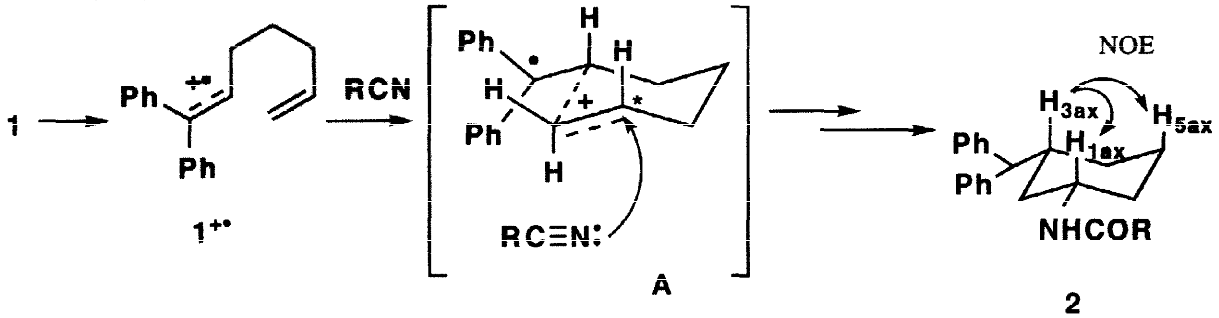
Scheme 1

In general, acetonitrile used as the solvent in photoinduced electron transfer reactions does not take place nucleophilic addition to radical cation species.[1, 3] However, we found that the highly stereoselctive photo-Ritter reaction occurs during the redox photosensitized electron transfer reaction of 1,1-diphenyl-1,6-heptadiene (**1**) in wet acetonitrile. Thus, a mixture of **1** (1×10^{-2} M) in acetonitrile containing H_2O (3×10^{-1} M), 1,4-dicyanobenzene (**DCNB**) (2.5×10^{-2} M) and phenanthrene (**P**) (0.5×10^{-2} M) was irradiated with a 100 W high-pressure mercury lamp through a $CuSO_4$ filter solution at room temperature for 15 min. Purification of the reaction mixture with HPLC (Develosil ODS-10, CH_3CN as eluent) provided *cis*-1-acetamido-3-(diphenylmethyl)cyclohexane (**2**)[4] in 90 % yield along with the anti-Markovnikov hydration product 1,1-diphenylhept-6-en-2-ol (**3**)[4] (2%) (Scheme **1**). The similar redox photosensitized electron transfer reaction of **1** in propionitrile, butyronitrile, or benzonitrile containing water gave the corresponding Ritter products **2b**,[4] **2c**,[4] and **2d**,[4] respectively, in moderate yields (Scheme **1**). The structural assignments

0040-4039/98/$19.00 © 1998 Elsevier Science Ltd. All rights reserved.
PII: S0040-4039(98)00431-6

including stereochemistry for **2a** - **2d** were effected by the extensive analyses of ^{1}H NMR, ^{13}C NMR, IR, and mass spectral data coupled with NOE experiments (Scheme **2**).

The highly *cis*-selective stereochemical outcome of the present photo-Ritter reaction may be explained that the cyclization of the intermediate **1**$^{+\bullet}$ proceeded through the favorable 6-membered chair-like transition state **A**, where the developing distonic cationic center [asterisked (*) carbon] was attacked simultaneously with the nitrile group from the peripheral (equatorial) direction (Scheme **2**).

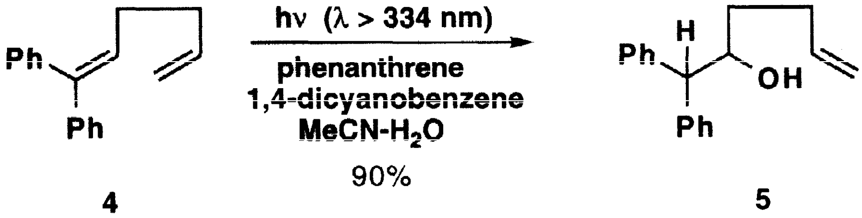


Scheme 2

As expected, the yields of the photo-Ritter reaction products decreased with increasing the water content in the reaction medium. For example, while **2a** was obtained in 90% yield by the reaction in acetonitrile containing 30 equiv. of H_2O (3 x 10^{-1} M in MeCN), 71 and 56% yields of **2a** were observed in acetonitrile containing 50 equiv.of H_2O (5 x 10^{-1} M in MeCN) and 100 equiv. of H_2O (1 M in MeCN), respectively.

Interestingly 1,1-diphenyl-1,5-hexadiene (**4**) underwent no photo-Ritter reaction but anti-Markovnikov hydration to give 1,1-diphenylhex-5-en-2-ol (**5**)^4 in 90% yield (Scheme **3**).^{1} The thermal Ritter reaction of **1** under the conventional conditions (H_2SO_4- AcOH in acetonitrile) gave none of **2a** but an ill-defined complex mixture.

The scope and limitaion of this photo-Ritter reaction of radical cation species are now in progress.



Scheme 3

References and Notes

1) a) Neunteufel, R. A.; Arnold, D, R. *J. Am. Chem. Soc.* **1973**, *95*, 4080-4081.
   b) Majima, T.; Pac, C.; Nakasone, A.; Sakurai, H. *J. Am. Chem. Soc.* **1981**, *103*, 4499-4508.
   c) Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1986**, *108*, 7356-7361.
   d) Hoffmann, U.; Gao, Y.; Pandey, B.; Klinge, S.; Warzecha, K.-D.; Krüger, C.; Roth, H. D. Demuth, M. *J. Am. Chem. Soc.* **1993**, *115*, 10358-10359.
   e) Heinemann, C.; Demuth, M. *J. Am. Chem. Soc.* **1997**, *119*, 1129-1130.
2) The non-stereoselective photo-Ritter reaction as a minor process has been reported: Cristol, S. J.; Dickenson, W. A.; Stanko, M. K. *J. Am. Chem. Soc.* **1983**, *105*, 1218-1220. See also de Lijser, H. J. P.; Arnold, D. R. *J. Org. Chem.* **1997**, *62*, 8432-8438, and the references cited therein.
3) The nucleophilic addition of acetonitrile to distonic cation radicals are reported.
   a) Mattes, S. L.; Farid, S. *J. Chem. Soc., Chem. Commun.* **1980**, 126-129.
   b) Zona, T. A.; Goodman, J. L. *Tetrahedron Lett.* **1992**, *33*, 6093-6096.
   c) Zona, T. A.; Goodman, J. L. *J. Am. Chem. Soc.* **1993**, *115*, 4925-4926.
4) Satisfactory ^{1}H NMR, ^{13}C NMR, IR, mass spectral , and high-resolution mass spectral data were obtained for this compound.