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PET Reactions of *cis*-Dibenzoylalkenes: An Efficient *trans*-Reduction of C═C bond

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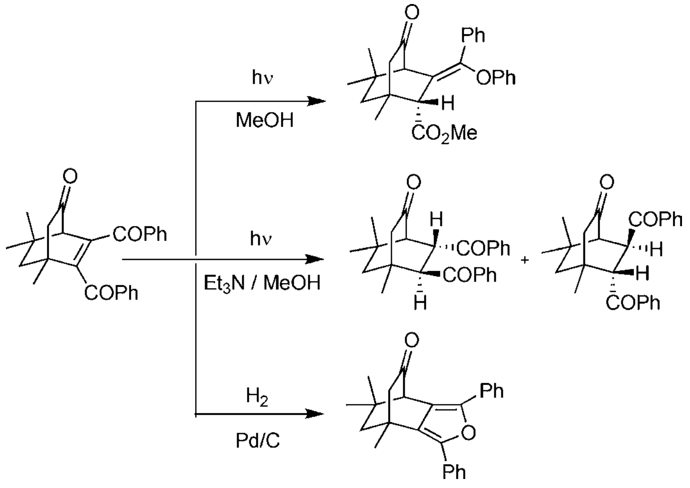
ABSTRACT



In contrast to its reaction under catalytic hydrogenation, the first instance of an exclusive and chemoselective *trans*-reduction of the ene part of derivatives of 5,6-dibenzoylbicyclo[2.2.2]oct-5-en-2-one has been reported under moderate photoinduced electron transfer (PET) conditions using triethylamine (TEA). In the absence of TEA, such molecules underwent 1,5-photophenyl migration yielding vinyl ketenes.

Photoinduced electron transfer (PET) reactions have gained immense popularity over the years as a means of promoting bimolecular photochemical reactions involving amines and triplet excited chromophores. Furthermore, since the seminal work of pioneers in the field like Peters,[1] Schuster,[2] and Mariano,[3] a comprehensive picture of the dynamics of the PET reaction involving amines has emerged. After electron transfer from the amine to the electronically excited acceptor the initially formed radical ions can give rise to a number of products depending upon the substrate.[4] We have previously reported the application of the PET reactions using triethylamine (TEA) for the synthesis of bicyclo[3.2.1]octanone skeleton **3** by the one-pot conversion of bicyclo[2.2.2]octenone **1** via tricyclo[3.3.0.0^{2,8}]octanone **2** (Scheme 1).[5] In contrast

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(1) (a) Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1982**, *104*, 6542. (b) Schaefer, C. G.; Peters, K. S. *J. Am. Chem. Soc.* **1980**, *102*, 7566.

(2) (a) Schuster, D. I.; Insogna, A. M. *J. Org. Chem.* **1991**, *56*, 1879. (b) Weir, D.; Scaiano, J. C.; Schuster, D. I. *Can. J. Chem.* **1988**, *66*, 2595.

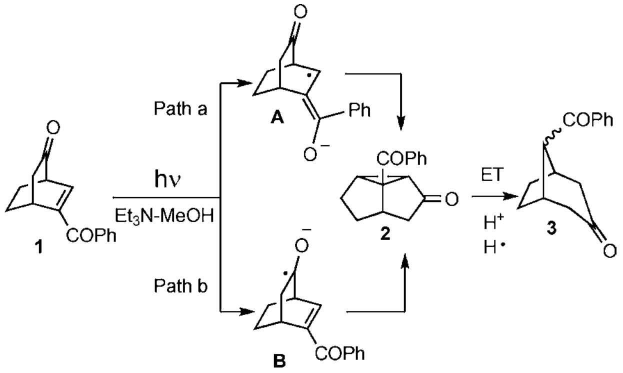
(3) (a) Yoon, U. C.; Kim, J. U.; Hasegawa, E.; Mariano, P. S. *J. Am. Chem. Soc.* **1987**, *109*, 4421. (b) Hasegawa, E.; Xu, W.; Mariano, P. S.; Yoon, U. C.; Kim, J. U. *J. Am. Chem. Soc.* **1988**, *110*, 8099. (c) Yoon, U. C.; Marino, P. S. *Acc. Chem. Res.* **1992**, *25*, 233.

(4) Recent reviews: (a) Cossy, J.; Belotti, D. *Tetrahedron* **2006**, *62*, 6459. (b) Oelgemöller, M.; Griesbeck, A. G. In *CRC Handbook of Organic Photochemistry and Photobiology*; Horsepool, W. M.,; Lenci, F., Eds.; CRC Press: Boca Raton, FL, 2004; p 84-1. (c) Cossy, J. In *Radicals in Organic Synthesis*; Renaud, P.,; Sibi, M. P., Eds.; Wiley-VCH: Weinheim, 2001; Vol. 1, p 229. (d) Albini, A.; Fagnoni, M.; Mella, M. *Pure Appl. Chem.* **2000**, *72*, 1321. (e) Santamaria, J. *Pure Appl. Chem.* **1995**, *67*, 141.

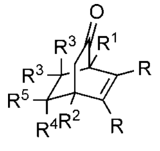
(5) Yadav, S.; Banerjee, S.; Maji, D.; Lahiri, S. *Tetrahedron* **2007**, *63*,

10.1021/ol901307v CCC: $40.75

Scheme 1. One-Pot Transformations of **1** to **3**



to general expectations that the triplet transformations of **1** to **2** would be retarded by the presence of TEA, a known enone triplet quencher, we found that the transformation to **3** was in general very efficient. The observation was rationalized on the basis of a mechanism based on initial formation of ketyl radicals **A** or **B** which then could generate **2** by back-electron transfer and bond migration followed by PET-mediated tandem bond migration of **2** to generate **3**. Such an electron transfer induced 1,2-acyl shift to give a tricyclo compound has been reported to occur from α,β-unsaturated aldehydes.[6]



4a-i
R = COPh

a: $R^1 = R^2 = R^3 = R^4 = R^5 = H$
b: $R^1 = R^3 = R^4 = R^5 = H$, $R^2 = OCH_3$
c: $R^1 = R^4 = R^5 = H$, $R^2 = R^3 = CH_3$
d: $R^1 = CH_3$, $R^2 = R^3 = R^4 = R^5 = H$
e: $R^1 = R^3 = R^4 = R^5 = H$, $R^2 = CH_3$
f: $R^1 = R^2 = CH_3$, $R^3 = R^4 = R^5 = H$
g: $R^1 = R^2 = R^4 = R^5 = H$, $R^3 = CH_3$
h: $R^1 = R^2 = R^3 = R^5 = H$, $R^4 = CH_3$
i: $R^1 = R^3 = R^4 = H$, R^2-R^5 = $(CH_2)_4$

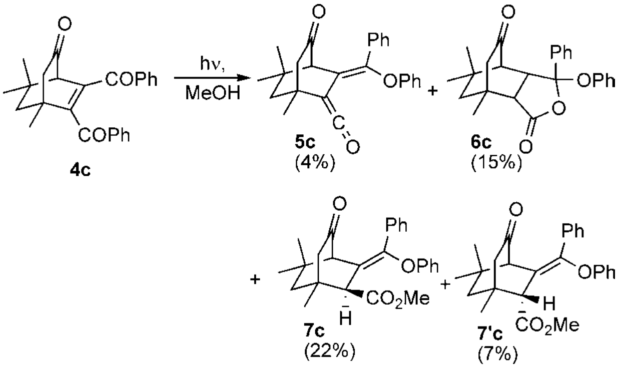
Figure 1. Dibenzoyl derivatives of bicyclo[2.2.2]octenone.

While on direct excitation **1** and its derivatives were efficiently transformed to the derivatives of tricyclo[3.3.0.0^{2,8}]-octanone **2**, derivatives of **4**[7a,b,8] (**4a**−**i**, Figure 1) with an additional benzoyl group at C-6 primarily underwent a regioselective 1,5-phenyl migration which is characteristic of *cis*-dibenzoylalkene chromophore, leading to vinyl ketenes of type **5c**.[9,10] The propensity of such 1,5-phenyl migration is known to be further accelerated by a rigid bicyclic frame which prevented the usual *cis*−*trans* isomerizations.[11] The solid-state photoreactions of these compounds provided a general and facile route to the regioselective 1,5-phenyl migration leading to first-time isolation and characterization of vinyl ketenes.[7b,8]

If **A** (Scheme 1) is the primary intermediate in such PET reactions, a 6-benzoyl substitution is likely to stabilize the radical by conjugation which in turn might behave differently. Because of the differential reactivities of **1** and **4** on direct excitation, we wished to explore such transformations of molecules of type **4** under PET condition.

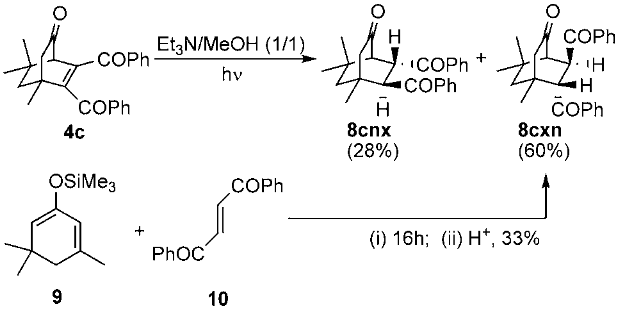
We started our present investigations by carrying out the solution-phase photolysis of **4c** (Scheme 2).[12] In benzene, the photoreaction gave a single ketene **5c**[8] (30%) and the lactone **6c** (12%). The ketene could be trapped if the reaction was carried out in MeOH, and along with **5c** (4%) and **6c** (15%), two diastereomeric esters **7c**[8] (22%) and **7′c** (7%) could also be isolated. The products were isolated and characterized on the basis of detailed analytical and spectral data. As stated previously, no tricyclic product was obtained from this reaction.

Scheme 2. Phototransformations of **4c** in MeOH



When the same reaction in MeOH was carried out with TEA, two isomeric 5-*endo*-6-*exo*- (**nx**) and 5-*exo*-6-*endo*-dibenzoyl (**xn**) derivatives of bicyclo[2.2.2]octanone (**8cnx** and **8cxn**) were obtained (Scheme 3) in an approximately

Scheme 3. PET Reduction of **4c**



10979.

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[10] (a) Griffin, G. W.; O'Connell, E. J. *J. Am. Chem. Soc.* **1962**, *84*, 4148. (b) Zimmermann, H. E.; Durr, H. G. C.; Lewis, R. G.; Bram, S. *J. Am. Chem. Soc.* **1962**, *84*, 4149. (c) Padwa, A.; Crumrine, D.; Shubber, R. A. *J. Am. Chem. Soc.* **1966**, *88*, 3064. (d) Rubin, M. B.; Sander, W. W. *Tetrahedron Lett.* **1987**, *28*, 5137.

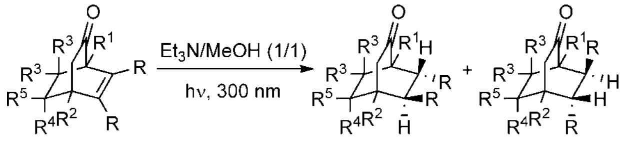
1:2 ratio.[13] Repeat runs of the reaction identified a 1/1 solution of TEA in MeOH as the best condition for such PET reductions. Interestingly, **8cxn** has been isolated as the only adduct (33%) from the Diels−Alder reaction of 1,5,5-trimethyl-2-trimethylsilyloxycyclohexa-1,3-diene (**9**) and (*E*)-1,4-diphenylbut-2-ene-1,4-dione (**10**).[14]

This present photoreduction of the double bond in general contrasts with the PET reactions of ketones and enones involving TEA, which has been reported to lead to a complex mixture of products via reduction, dimerization, and addition.[4a,15]

Another important aspect of the reaction was the formation of the isomer **8cnx** from **4c** which otherwise could not be obtained from the Diels−Alder reaction between **9** and **10**.

The generality of such double-bond photoreduction was confirmed from the reactions of **4a**,**b**,**d**−**h** under PET conditions. All of these compounds underwent exclusive reduction of the double bonds under similar reaction conditions (Scheme 4).[14] In all cases, the *5-exo-6-endo* derivatives (**xn**) were either the major or the only product formed from the reactions. All new compounds were characterized on the basis of their analytical and spectral data.

Scheme 4. PET Reactions of **4a**−**i**



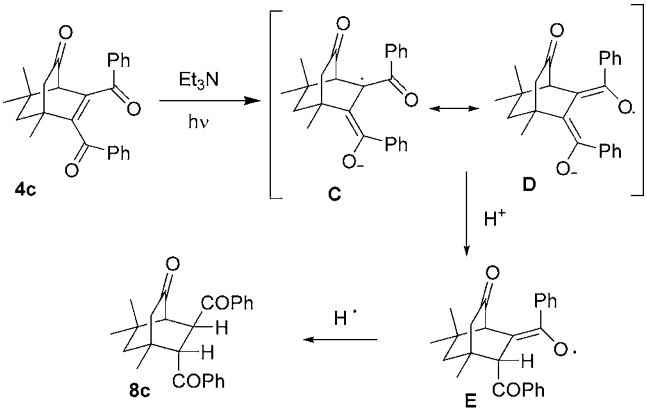
4a-i
R =COPh

8a-i nx	**8a-i xn**
a: 27% (37%)	**a**: 57% (25%)
b: 20% (42%)	**b**: 65% (13%)
c: 28% (0%)	**c**: 60% (33%)
d: 0% (17%)	**d**: 72% (31%)
e: 20% (43%)	**e**: 65% (15%)
f: 0% (39%)	**f**: 90% (19%)
g: 13% (0%)	**g**: 83% (31%)
h: 20% (20%)	**h**: 50% (0%)
i: 21% (58%)	**i**: 70% (27%)

[a] The yields in parentheses refer to the reported yields of the products from Diels−Alder reactions of **10** with substituted cyclohexadienes (ref 14).

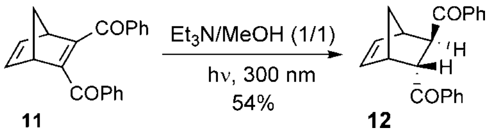
The 1,5-phenyl migration from the *cis*-DBE moiety on direct irradiation has been reported to originate from the singlet states at least for the nonrigid systems,[16] whereas for a rigid framework, triplet states have been found to be the reactive intermediates for such photomigrations.[11] In the case of **4c**, quenching of vinylketene formation by anthracene (E_t = 42 kcal/mol) confirmed involvement of triplet in its excited state. Since under PET conditions addition of TEA quenched the formation of vinylketene from **4**, electron transfer from TEA to their triplets appeared to be the reaction-initiating step. Similar to **A** in Scheme 1, radical cation **C** (Scheme 5) thus formed will be better stabilized by delocalization giving a ketyl radical cation **D** which then by proton abstraction followed by hydrogen radical abstraction either from the solvent or from the amine radical anion[17] would give the thermodynamically more stable *trans*-hydrogenated diastereomers of **8c**.

Scheme 5. Probable Route for PET Reduction of **4c**



That the radical anion **B** (Scheme 1) does not have any role in these PET-reduction processes was confirmed from the photoreaction of **11** in the presence of TEA. Compound **11** has been reported to yield a quadricyclane via an intramolecular [2 + 2] cycloaddition during solution-phase photolysis.[11a] Under PET conditions, **11** yielded the *trans*-hydrogenated product **12**[18] in good yield (Scheme 6).

Scheme 6. PET Reaction of **12**



11   **12**

Metal-catalyzed selective hydrogenation of the double bond of cyclic enones is known in the literature.[19] The present method under PET condition reports a very moderate method of *trans*-reduction of the *cis*-DBE system.

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(11) (a) Lahiri, S.; Dabral, V.; Chauhan, S. M. S.; Chakachery, E.; Kumar, C. V.; Scaiano, J. C.; George, M. V. *J. Org. Chem.* **1980**, *45*, 3782. (b) Murty, B. A. R. C.; Kumar, C. V.; Dabral, V.; Das, P. K.; George, M. V. *J. Org. Chem.* **1984**, *49*, 4165. (c) Lohray, B. B.; Kumar, C. V.; Das, P. K.; George, M. V. *J. Org. Chem.* **1984**, *49*, 4647. (d) Barik, R.; Bhattacharya, K.; Das, P. K.; George, M. V. *J. Org. Chem.* **1986**, *51*, 3420.

(12) A degassed solution of **4c** (250 mg, 0.67 mmol) in 50 mL of MeOH was irradiated in a Rayonet photochemical reactor using lamps of 300 nm wavelength for 3.5 h. The solvent was removed under reduced pressure, and the residual mixture was purified over a column of silica gel to give pure products.

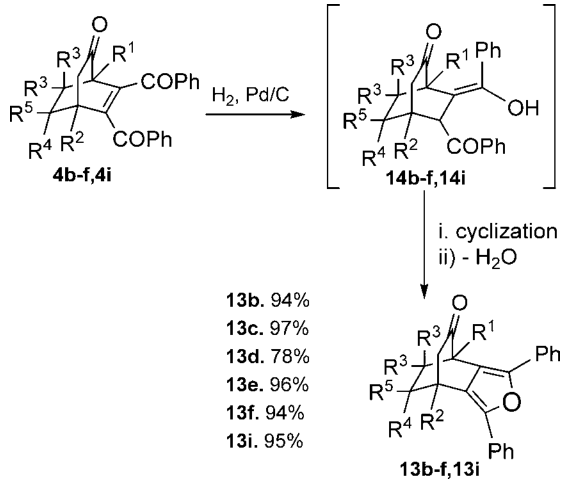
(13) A degassed solution of **4c** (150 mg, 0.403 mmol) in 50 mL of 1:1 TEA−MeOH was irradiated in a Rayonet photochemical reactor using lamps of 300 nm wavelength for 1 h. The volatile components were then removed under reduced pressure, and the residue was chromatographed to yield pure products.

(14) Lahiri, S.; Yadav, S.; Banerjee, S.; Patil, M. P.; Sunoj, R. B. *J. Org. Chem.* **2008**, *73*, 435.

Since the reductions of the alkene part in **4a−h**,**i** were so efficient under the PET conditions, we wished to compare these results with those under catalytic hydrogenation conditions.

Compounds **4b−f**,**i** on hydrogenation using Pd/C catalyst underwent quantitative reductive cyclization to furan derivatives **13b−f**,**i** presumably via the 1,4-hydrogenated intermediate **14b−f**,**i** (Scheme 7).[20] Reductive generation of such enolates under hydrogenation conditions are known to participate in intramolecular bond formation via carbonyl addition.[21]

Scheme 7. Catalytic Hydrogenation of **4b−f**,**i**



In conclusion, we have reported here the first instance of selective *trans*-reduction of *cis*-dibenzoylalkenes employing a PET process. While such reactions of TEA with enones generally gave complex mixtures, in the present examples under very mild conditions, the thermodynamically stable *trans*-alkanes were produced in high yields which were otherwise very difficult to prepare. Future studies will be devoted to exploring the generality of these reactions for other such ene−dione systems.

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Supporting Information Available: Full ^{1}H and ^{13}C NMR spectroscopic data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Cossy, J.; Furet, N.; BouzBouz, S. *Tetrahedron* **1995**, *51*, 11751.

(18) Adams, R.; Gold, M. H. *J. Am. Chem. Soc.* **1940**, *62*, 56.

(19) For examples of selective catalytic hydrogenation of enones, see: (a) Tuttle, J. B.; Ouellet, S. G.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2006**, *128*, 12662. (b) Keinan, E.; Greenspoon, N. Partial Reduction of Enones, Styrenes and Related Systems. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: New York, 1991; Vol. VIII, p 523.

(20) To a solution of **4c** (100 mg) in MeOH (12 mL), Pd/C (10 mg) was added and to the flask a ballon filled with hydrogen gas was attached. The mixture was then stirred for 1h after which the solution was filtered and the solvent removed to give a colorless solid of **13c** (97 mg, 97%).

(21) (a) Huddleston, R. R.; Krische, M. J. *Org. Lett.* **2003**, *5*, 1143. (b) Jang, H.-Y.; Krische, M. J. *Eur. J. Org. Chem.* **2004**, 3953.