Solid-state photolysis of sterically congested *cis*-1,2-dibenzoylalkenes: isolation and characterization of vinylketenes

Mithu Chanda, Dwijendralal Maji and Saswati Lahiri*

Department of Organic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700032, India.
E-mail: ocsl@mahendra.iacs.res.in

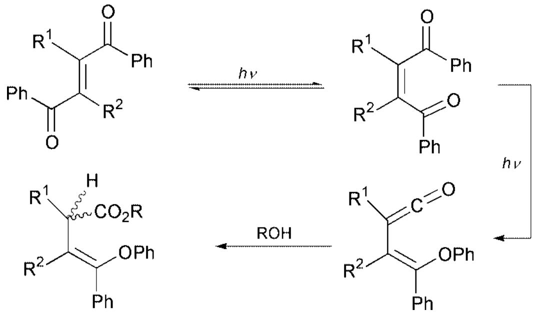
Received (in Cambridge, UK) 8th November 2000, Accepted 12th February 2001
First published as an Advance Article on the web 28th February 2001

Hitherto non-isolable vinylketenes from the solid state photolysis of *cis*-1,2-dibenzoylalkene compounds have been isolated and characterized and their stabilities were found to be enhanced with the extent of steric congestion in the molecules.

Formation of vinylketenes from the photoreactions of *cis*-1,2-dibenzoylethylenes was first speculated in 1962[1] (Scheme 1). Its intermediacy was confirmed later from a strong peak for $\nu_{C=C=O}$ at 2103 cm^{-1} in the IR spectrum of the photolyzed reaction mixture.[2] Such photoinduced intramolecular phenyl migration from carbon to the proximate oxygen is a general reaction route for *cis*-1,2-dibenzoylalkene chromophore and has been observed in tetrabenzoylethylene[3] as well as in other *cis*-1,2-dibenzoylalkene derivatives.[4,5] In unsymmetrical derivatives, such migrations have been found to take place from the benzoyl group attached to the more crowded olefinic carbon atom.[1,4*a*,*b*,5] However, in our work with 5,6-dibenzoyl-4-methoxybicyclo[2.2.2]oct-5-en-2-one (**1**) such migration was observed to occur from both the benzoyl groups in solution, whereas in solid state, only the expected vinylketene (**1K**) was identified.[6] In all of these cases the intermediate vinylketenes have so far been neither isolated nor characterized fully because of their instability. The vinylketene **1K** was found to be fairly stable in cyclohexane solution at 20 °C. It took almost 48 h for the total disappearance of the ketene band at 2100 cm^{-1}. Such an observation encouraged us to take up the present project to enhance the steric congestion in such molecules and try to isolate the intermediate vinylketenes and characterize them.

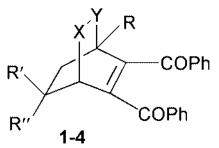
In this attempt, the residue from the solid-state photoreaction of **1** was carefully chromatographed on a silica gel column.[7] Ketene **1K** as a pale-yellow solid (25%) and the starting compound **1** (70%) were separated from this reaction mixture. The spectral data of **1K** agreed well with the proposed structure. Since all attempts for recrystallization led to its decomposition, elemental analysis for **1K** could not be performed. However, its structure was finally confirmed by trapping it with MeOH which gave 4-methoxy-6-(phenoxyphenylmethylene)-5-*exo*-carbomethoxybicyclo[2.2.2]octan-2-one (**1E**).

To increase the persistency of such vinylketenes, we decided to enhance steric congestion in the molecule and hence prepared compound **2** with a methyl group at the bridgehead. Solid-state photolysis of **2** and chromatography of the photolyzed residue gave white crystals of the corresponding vinylketene **2K** (27%) whose analytical and spectral data were in agreement with the proposed structure. Further elution gave back unreacted starting material **2** (68%). The ketene **2K** was stable at rt and could be trapped with MeOH only at elevated temperature (~40 °C) to give 4-methyl-6-(phenoxyphenylmethylene)-5-*exo*-carbomethoxybicyclo[2.2.2]octan-2-one (**2E**) as the major product along with its 5-*endo* epimer (**2E′**) in minor yield.

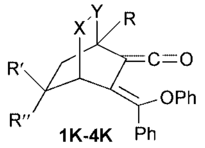


Scheme 1

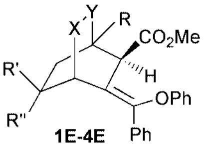
The preference of photo-phenyl migration in *cis*-1,2-dibenzoylalkene chromophore from the more crowded olefinic carbon atom in the solid state, was further confirmed from the solid state photoreaction of compound **3**. Chromatography of the reaction mixture yielded the vinylketene **3K** (35%), unreacted starting material **3** (37%) and an unidentified gummy material (25%). The ketene **3K** was found to be less stable than its isomer **2K** and on stirring with MeOH at rt it yielded 1-methyl-5-(phenoxyphenylmethylene)-6-*exo*-carbomethoxybicyclo[2.2.2]octan-2-one (**3E**).



1-4



1K-4K



1E-4E

Where,
1, 1K, 1E : X = CO; Y = CH_2; R = OMe; R′ = R″ = H
2, 2K, 2E : X = CO; Y = CH_2; R = Me; R′ = R″ = H
3, 3K, 3E : X = CH_2; Y = CO; R = Me; R′ = R″ = H
4, 4K, 4E : X = CO; Y = CH_2; R = R′ = R″ = Me

Addition of nucleophiles to ketenes is thought to occur in the plane of the ketene and the approach occurs from the least sterically hindered site of the ketene.[8,9] Increasing the steric congestion in a molecule thus could remarkably enhance persistency of vinylketenes and retard the nucleophilic addition to it. This was further confirmed from the solid state photolysis of 5,6-dibenzoyl-4,7,7-trimethylbicyclo[2.2.2]oct-5-en-2-one (**4**), which gave white crystals of the vinylketene **4K** (28%) along with the unreacted starting material (65%). Even under atmospheric conditions, solid **4K** could be stored without decomposition for a long time and its cyclohexane solution was stable at rt for more than 5 days. Addition of MeOH to **4K** took place only under refluxing conditions to yield 4,7,7-trimethyl-6-(phenoxyphenylmethylene)-5-*exo*-carbomethoxybicyclo-[2.2.2]octan-2-one (**4E**).

The ketene bands of **1K–4K** appeared near 2100 cm^{-1} in the IR spectrum. The ^{1}H-NMR spectra of these compounds were very similar to their parent molecules but their ^{13}C-NMR data were found to be much more useful (Table 1). In ^{1}H-NMR, the *endo*-protons around δ 3 ppm appeared as doublets for **1E, 2E** and **4E** and as a singlet for **3E** (Table 1).

DOI: 10.1039/b009013l

Table 1 Characteristic data for **1K–4K** and **1E–4E**

Starting compound[a]	Products[b] (mp/°C)	Yield (%)	IR/cm^{-1} $\nu_{C=C=O}$	^{1}H-NMR/ppm $\delta_{Bridgehead}$	$\delta_{Bridgehead}$	^{13}C-NMR/ppm δ_{C+O}	δ_{+C+O}	δ_{C+C+O}	$\delta_{+C\text{-}OPh}$
1	**1K**[c] (157)	85[d]	2103	3.6 (m)		207.0	199.4	34.9	155.7
2	**2K** (187)	84[d]	2100	3.65 (t, *J* 3 Hz)		210.5	202.3	34.2	155.7
3	**3K** (122)	55[d]	2092	3.38 (t, *J* 2.4Hz)		210.0	200.2	40.8	155.8
4	**4K** (125)	82[d]	2100	3.21 (s)		210.3	208.9	34.4	155.7
1K	**1E** (41)	93[e]		3.45 (m)	3.95 (d, *J* 2 Hz)				
2K	**2E** (125)	59[e]		3.46 (t, *J* 3 Hz)	3.46 (t, *J* 1.5 Hz)				
	2E′(132)	28[e]		3.44 (t, *J* 3 Hz)	3.52 (d, *J* 1.5 Hz)				
3K	**3E** (158)	89[e]		3.3 (m)	3.6 (s)				
4K	**4E** (156)	90[e]		3.06 (s)	3.26 (d, *J* 1.5 Hz)				

[a] Compounds **1–4**, for the first time were prepared following reported procedures.[5,10] [b] Elemental analyses have been performed for all compounds excepting **1K**. [c] Unstable to prepare analytical sample. [d] Based on recovered starting materials. [e] Isolated yields.

In summary, we report here the first isolation and characterization of the intermediate vinylketene formed by photo-phenyl migration in *cis*-dibenzoylalkenes. In the solid state, the migration always occurred from the more crowded center to the less crowded one. By controlling the degree of steric congestion in the molecule, the stability of these vinylketenes can remarkably be enhanced.

Financial support from DST, India is gratefully acknowledged.

Notes and references

1 (*a*) G. W. Griffin and E. J. O'Connell, *J. Am. Chem. Soc.*, 1962, **84**, 4148; (*b*) H. E. Zimmerman, H. G. C. Dürr, R. G. Lewis and S. Bram, *J. Am. Chem. Soc.*, 1962, **84**, 4149.

2 A. Padwa, D. Crumrine and R. A. Shubber, *J. Am. Chem. Soc.*, 1966, **88**, 3064.

3 M. B. Rubin and W. W. Sander, *Tetrahedron Lett.*, 1987, **28**, 5137.

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

5 R. Singh, A. Sinha and S. Lahiri, *J. Chem. Res. (S)*, 1992, 372.

6 D. Maji, R. Singh, G. Mostafa, S. Roy and S. Lahiri, *J. Org. Chem.*, 1996, **61**, 5165.

7 In a typical solid state photoreaction, a suspension of the compound (0.5–1 g) in distilled water (150 ml) was irradiated with stirring using a Hanovia medium pressure 450 W lamp and a pyrex filter for ~ 35 h. The suspension was then extracted with CH_2Cl_2 and the residue obtained after removal of solvent was chromatographed on a silica gel column (60–120 mesh). The ketene was eluted with a mixture of ethyl acetate (5–10%) in petroleum ether (bp 60–80 °C).

8 T. T. Tidwell, *Acc. Chem. Res.*, 1990, **23**, 273.

9 C. O. Kappe, R. A. Evans, C. H. L. Kennard and C. Wentrup, *J. Am. Chem. Soc.*, 1991, **113**, 4234.

10 S. Lahiri and R. Singh, *Indian J. Chem.*, 1980, **28B**, 860.