JOC Article

Enhanced Diastereoselectivity via Confinement: Diastereoselective Photoisomerization of 2,3-Diphenyl-1-benzoylcyclopropane Derivatives within Zeolites

J. Sivaguru,[†] Raghavan. B. Sunoj,[‡] Takehiko Wada,[§] Yumi Origane,[‖] Yoshihisa Inoue,[§,‖] and V. Ramamurthy*,[†]

Department of Chemistry, Tulane University, New Orleans, Louisiana 70118, Department of Chemistry, Indian Institute of Technology, Bombay, Mumbai 400076, India, Department of Molecular Chemistry and PRESTO (JST), Osaka University, 2-1 Yamada-oka, Suita 565-0871, Japan, and ICORP Entropy Control Project, JST, 4-6-3 Kamishinden, Toyonaka 560-0085, Japan.

murthy@tulane.edu

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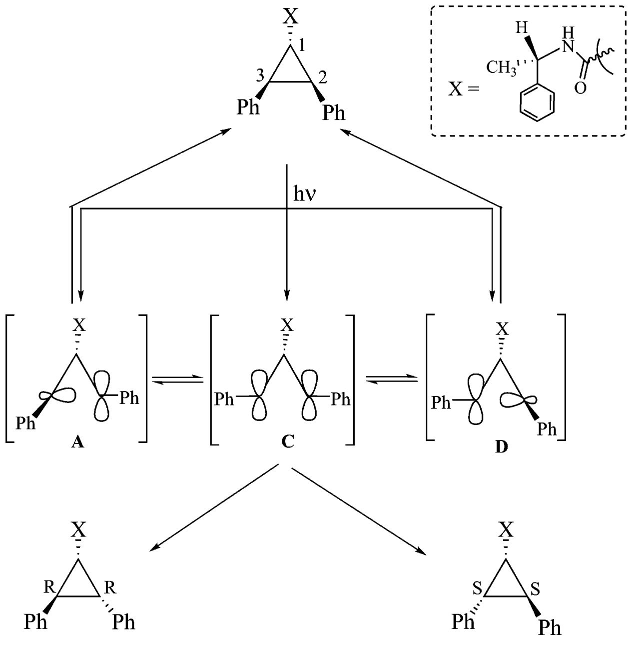
Photochemistry of optically pure *trans*-2,3-diphenyl-1-benzoylcyclopropane has been examined in isotropic solution and within zeolites. Results suggest that it isomerizes by cleavage of either the C_1-C_2 or C_1-C_3 bond. From the perspective of chiral induction, photoisomerization of *cis*-2,3-diphenyl-1-benzoylcyclopropane derivatives with chiral auxiliaries placed at the *meta* and *para* positions of the benzoyl group have been examined both in isotropic solution and within zeolites. Whereas in isotropic solution the chiral auxiliaries placed at the *meta* position exhibit very little influence during the conversion of triplet *cis*-2,3-diphenyl-1-benzoylcyclopropane derivatives, they have significant influence within zeolites. For example, α-methyl benzylamine placed at the *meta* position of the benzoyl group (via an amide bond) yields the *trans* isomer with a diastereoselectivity (de) of 71% within NaY zeolite, whereas in solution no de is obtained. The chiral induction process within zeolites depends on the nature of the alkali ion and on the presence of water. Results suggest that the chiral auxiliary is able to control the bond being cleaved (C_1-C_2 vs. C_1-C_3 bond) within a zeolite, but it is unable to do so in an isotropic solution.

Introduction

By employing optically pure *trans*-2,3-diphenylcyclopropane-1-carboxylic acid derivatives, we have recently established that the photoisomerization of these systems in the triplet state and excited singlet state within zeolites occurs via C_2-C_3 bond cleavage.[1] This suggested that chiral selectivity in the product *trans* isomer from the excited *cis* isomer must occur at the stage of ring closure of the 1,3-diradical/zwitterionic intermediate (Scheme 1). By employing several chiral auxiliaries, we have shown that one could achieve significant chiral induction in the *trans* isomer upon direct excitation and triplet sensitization of the *cis*-2,3-diphenylcyclopropane-1-carboxylic acid derivatives included within zeolites. Results clearly showed that the chiral auxiliaries could influence the mode of ring closure of the 1,3-diradical/zwitterionic intermediate.

Zimmerman and co-workers have previously established that upon direct excitation photochemical isomerization of *cis*-2,3-diphenyl-1-benzoylcyclopropane proceeds from the triplet excited state with near unit quantum yield.[2] By employing different aryl groups at 2- and 3-positions they established that the geometric isomerization occurs by cleavage of either the C_1-C_2 or C_1-C_3 bond. Our interest in this system derives from the fact that the photoproduct the *trans*-2,3-diphenyl-1-

SCHEME 1



[†] Tulane University.

[‡] Indian Institute of Technology.

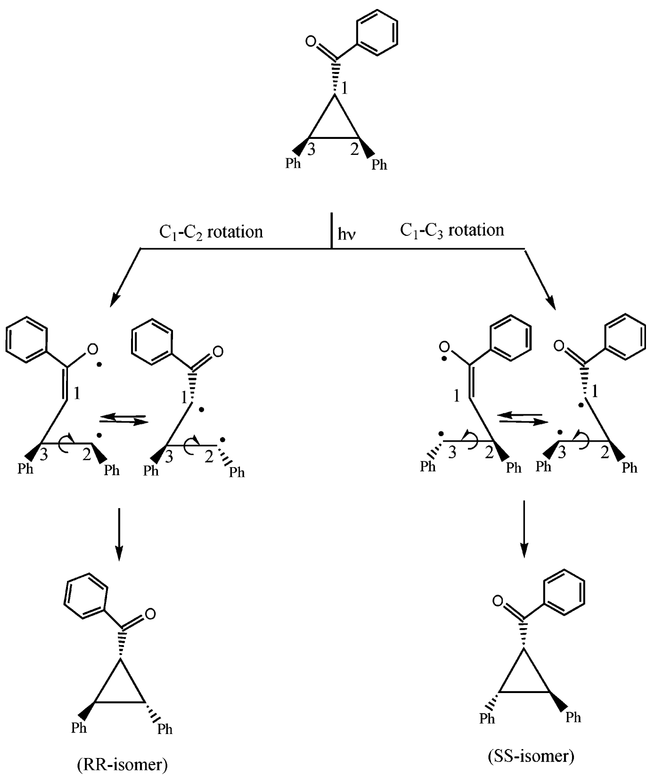
[§] Osaka University.

[‖] ICORP Entropy Control Project, JST.

(1) Sivaguru, J.; Shichi, T.; Ramamurthy, V. *Org. Lett.* **2002**, *4*, 4221−4224.

10.1021/jo049697n CCC: $27.50

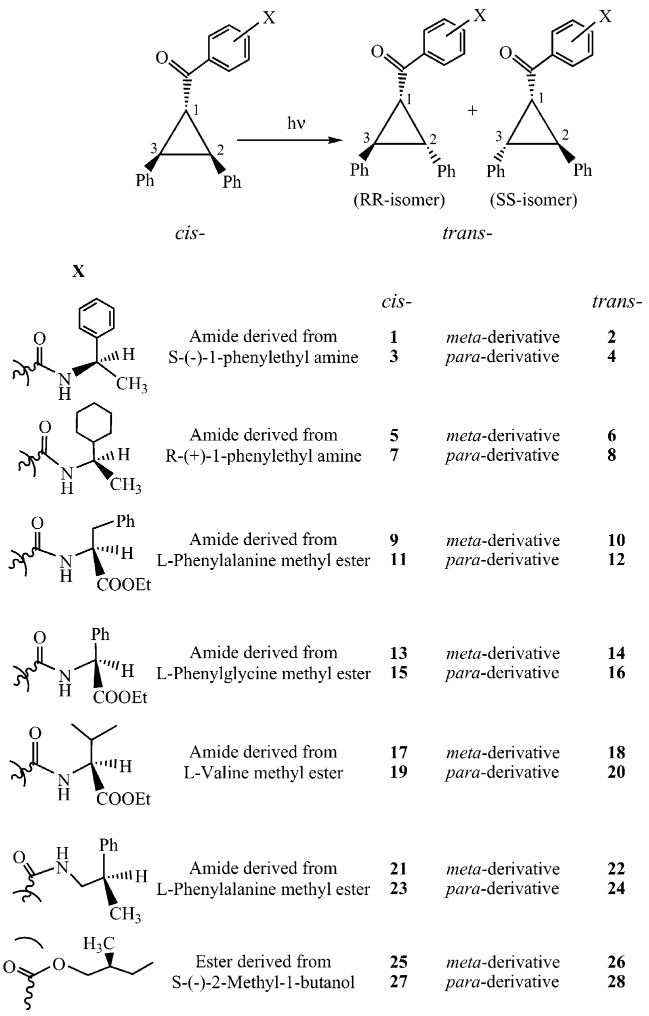
SCHEME 2



benzoylcyclopropane is chiral.[3] As per the above mechanism the chiral selectivity in the product *trans*-2,3-diphenyl-1-benzoylcyclopropane must occur at the stage of bond fragmentation (Scheme 2).

Depending upon which bond is cleaved, C_1-C_2 or C_1-C_3, either the RR or SS isomer would be formed. In the absence of chiral influence there is no selectivity in the bond being cleaved and therefore the enantiomeric excess (ee) in the product *trans* isomers (RR and SS) is expected to be zero. Solution results are consistent with this mechanism. In solution even a chiral inductor does not bring about any enantioselectivity. On the basis of the results obtained with *cis*-2,3-diphenylcyclopropane-1-carboxylic acid derivatives it was not clear whether a chiral auxiliary would influence the mode of cleavage (C_1-C_2 vs C_1-C_3) in *cis*-2,3-diphenyl-1-benzoylcyclopropane systems. This prompted us to examine the excited-state behavior of several *cis*-2,3-diphenyl-1-benzoylcyclopropane derivatives appended with chiral auxiliaries both in solution and within zeolites. The systems examined and their photoproducts are listed in Scheme 3. The compounds are identified on the basis of the geometrical relationship (*cis* and *trans*) between the two phenyl groups at C_2 and C_3 carbons and the stereochemical relationship (R and S) between them taking the C_1 carbon into account. The results presented below demonstrate that a chiral auxiliary can influence the mode of cleavage (C_1-C_2 vs C_1-C_3) and functions much better within a zeolite than in an isotropic solution. By placing the chiral auxiliary at *meta* and *para* positions of the benzoyl group we establish that the effectiveness of a chiral auxiliary depends on its proximity to the reaction site. The examples provided here emphasize the importance of using "dry" zeolites in achieving asymmetric induction during photochemical reactions. To verify the assumption concerning the mechanism of photoisomerization (occurring via cleavage of C_1-C_2 or C_1-C_3 and not through C_2-C_3 cleavage) we have examined the photochemistry of optically pure *trans*-2,3-diphenyl-1-benzoylcyclopropane. Results of this study are presented first.

SCHEME 3



X	*cis-*		*trans-*
Amide derived from S-(-)-1-phenylethyl amine	**1**	*meta*-derivative	**2**
	3	*para*-derivative	**4**
Amide derived from R-(+)-1-phenylethyl amine	**5**	*meta*-derivative	**6**
	7	*para*-derivative	**8**
Amide derived from L-Phenylalanine methyl ester	**9**	*meta*-derivative	**10**
	11	*para*-derivative	**12**
Amide derived from L-Phenylglycine methyl ester	**13**	*meta*-derivative	**14**
	15	*para*-derivative	**16**
Amide derived from L-Valine methyl ester	**17**	*meta*-derivative	**18**
	19	*para*-derivative	**20**
Amide derived from L-Phenylalanine methyl ester	**21**	*meta*-derivative	**22**
	23	*para*-derivative	**24**
Ester derived from S-(-)-2-Methyl-1-butanol	**25**	*meta*-derivative	**26**
	27	*para*-derivative	**28**

Results and Discussion

The stereoisomers (RR and SS) of *trans*-2,3-diphenyl-1-benzoylcyclopropane were obtained in pure form by preparative HPLC (Chiralcel OJ-R column). The absolute configuration of the pure isomers (RR and SS) of *trans*-2,3-diphenyl-1-benzoylcyclopropane, isolated by HPLC, was determined by comparing the specific rotation with that reported for pure *trans*-2,3-diphenyl-1-benzoylcyclopropane.[4] The sample collected as peak B (second peak in Chiralpak AD-RH column) showed a specific rotation

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(2) (a) Zimmerman, H. E.; Flechtner, T. W. *J. Am. Chem. Soc.* **1970**, *92*, 6931–6935. (b) Zimmerman, H. E.; Hixson, S. S.; McBride, E. F. *J. Am. Chem. Soc.* **1970**, *92*, 2000–2014. (c) Zimmerman, H. E.; Moore, C. M. *J. Am. Chem. Soc.* **1970**, *92*, 2023–2031.

(3) Chong, K. C. W.; Sivaguru, J.; Shichi, T.; Yoshimi, Y.; Ramamurthy, V.; Scheffer, J. R. *J. Am. Chem. Soc.* **2002**, *124*, 2858–2859.

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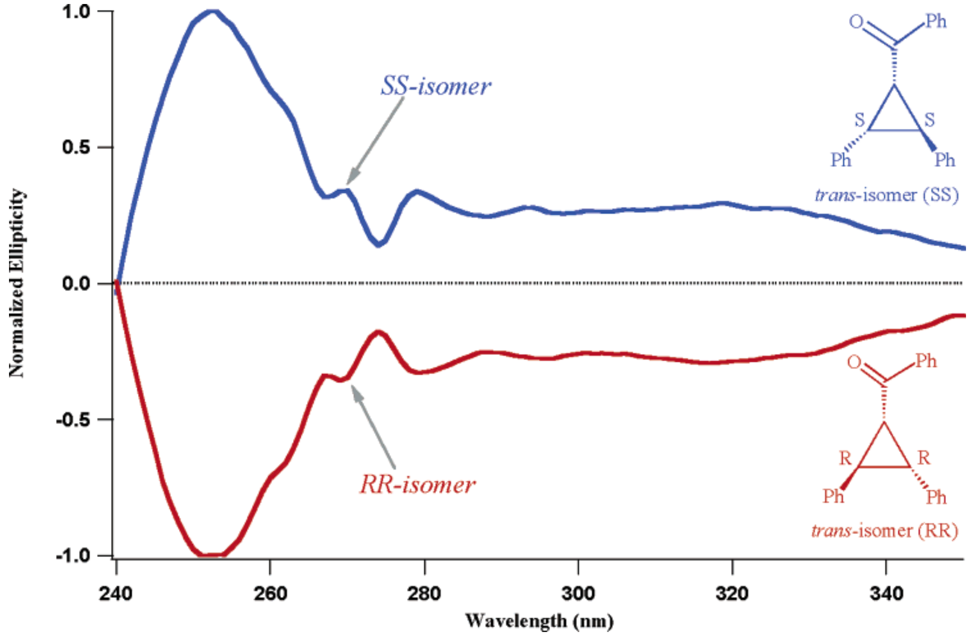


FIGURE 1. CD spectra of *trans*-2,3-diphenyl-1-benzoylcyclopropane (RR isomer) and *trans*-2,3-diphenyl-1-benzoylcyclopropane (SS isomer).

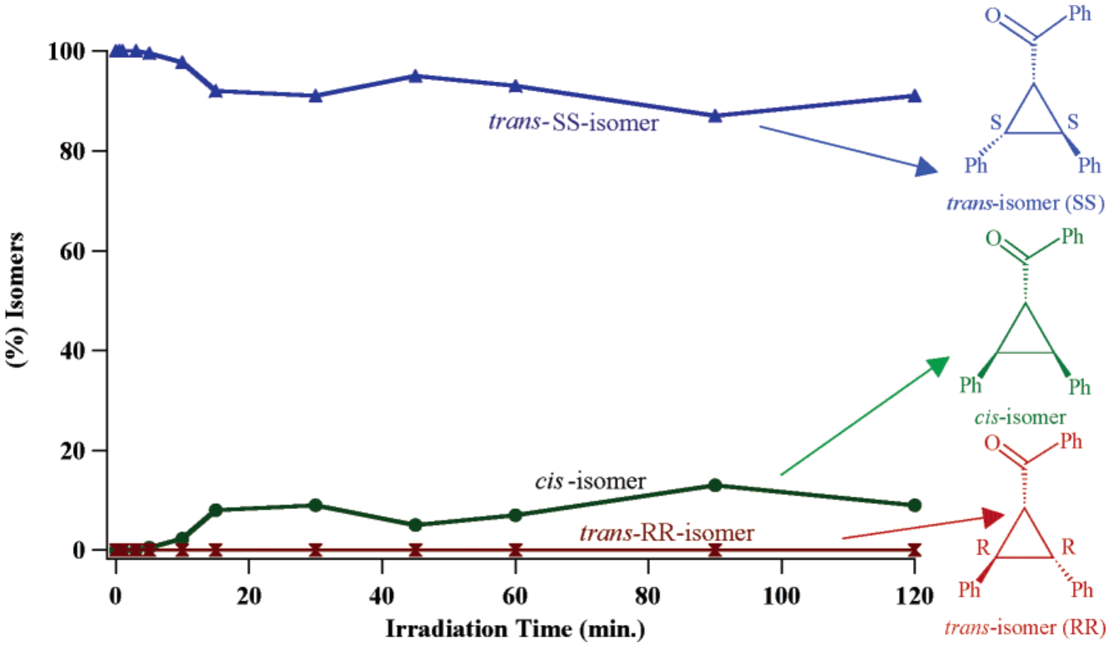


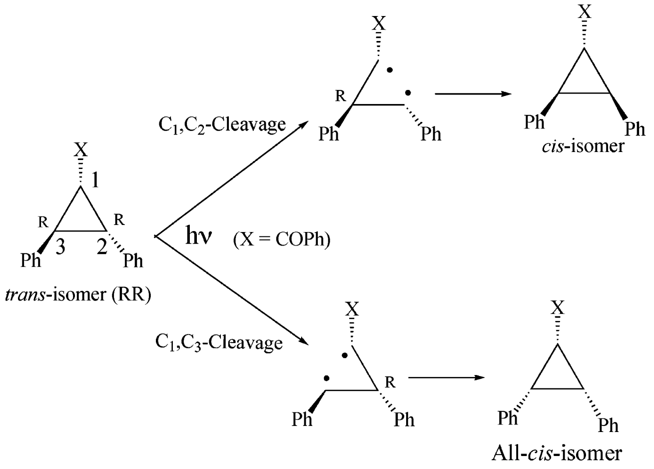
FIGURE 2. Product distribution with respect to time of direct excitation of *trans*-2,3-diphenyl-1-benzoylcyclopropane (SS isomer) in methylene chloride/hexane solution. Note that *trans*-2,3-diphenyl-1-benzoylcyclopropane (RR isomer) is not formed even after prolonged irradiation.

of −124° ($[\alpha]_D$) at 18 °C in dichloromethane solvent, and this corresponded to the RR isomer (lit. $[\alpha]^{25}_D$ −136° in dichloromethane).[4] As shown in Figure 1 enantiomeric *trans*-2,3-diphenyl-1-benzoylcyclopropane (RR isomer) and *trans*-2,3-diphenyl-1-benzoylcyclopropane (SS isomer) showed mirror-image circular dichroism spectra in dichloromethane.

Photoisomerization of *trans*-2,3-diphenyl-1-benzoylcyclopropane (SS isomer) by direct and sensitized irradiation was examined both in solution and within zeolites. The photochemistry of *trans*-2,3-diphenyl-1-benzoylcyclopropane (SS isomer) discussed below is also applicable to *trans*-2,3-diphenyl-1-benzoylcyclopropane (RR isomer). To conserve space, results of *trans*-2,3-diphenyl-1-benzoylcyclopropane (RR isomer) are not presented.

Direct irradiation (Pyrex tube) in solution was performed by dissolving ~5 mg of *trans*-2,3-diphenyl-1-benzoylcyclopropane (SS isomer) in 0.5 mL of dichloromethane and 15 mL of hexane. The relative ratios of the stereoisomers formed from *trans*-2,3-diphenyl-1-benzoylcyclopropane (SS isomer) as a function of irradiation time are plotted in Figure 2. As illustrated in Figure 2, irradiation of *trans*-2,3-diphenyl-1-benzoylcyclopropane (SS isomer) in solution gave only *cis*-2,3-diphenyl-1-

SCHEME 4



benzoylcyclopropane as the primary product (see Supporting Information for representative HPLC traces). Prolonged irradiation resulted in low mass balance as a result of side reactions. Irradiation of *trans*-2,3-diphenyl-1-benzoylcyclopropane (SS isomer) included within NaY zeolite (loading level 1 molecule per 10 supercages) gave only *cis*-2,3-diphenyl-1-benzoylcyclopropane (see Supporting Information for representative HPLC traces). Even after 1 h of irradiation, *trans*-2,3-diphenyl-1-benzoylcyclopropane (RR isomer) was not detected within LiY, NaY, KY, RbY, and CsY (see Supporting Information for data). As shown in Scheme 4 cleavage of the C_1-C_2 or C_1-C_3 bond would not allow interconversion between the *trans*-stereoisomers RR and SS. The only isomers expected from *trans*-2,3-diphenyl-1-benzoylcyclopropane (RR isomer) are *cis* and *all-cis*. In our case, the latter was not obtained. The fact that both in solution and in zeolites only *cis*-2,3-diphenyl-1-benzoylcyclopropane is obtained as the primary photoproduct from *trans*-2,3-diphenyl-1-benzoylcyclopropane (RR isomer) suggests that the photoisomerization proceeds via cleavage of the C_1-C_2 or C_1-C_3 bond. The above observations are consistent with the original suggestion by Zimmerman and Flechtner that the photoiosmerization in the case of 2,3-diphenyl-1-benzoylcyclopropane proceeds via cleavage of the C_1-C_2 or C_1-C_3 bond.

An additional point we wish to address is the enrichment of the *trans* isomer at the photostationary state of 2,3-diphenyl-1-benzoylcyclopropane. During excitation in solution and in zeolites, the photostationary state (*cis*:*trans*) was close to 15:85 within a zeolite and 5:95 in solution.[2] These numbers are different from the ones obtained in the case of 2,3-diphenylcyclopropane-1-carboxylic acid derivatives. For example, upon triplet sensitization α-methylbenzyl amide of 2,3-diphenylcyclopropane-1-carboxylic acid gave a photostationary state of 45:55 (*cis*:*trans*). The high *trans* content in the photostationary state (85% in zeolite and 95% in solution) during excitation of 2,3-diphenyl-1-benzoylcyclopropane, we believe, is due to steric hindrance in the intermediate diradical. A closer inspection of the diradical intermediates involved in the photoreaction of *cis*-2,3-diphenyl-1-benzoylcyclopropane (Scheme 5) shows that β-cleavage would result in the diradical intermediate **DR1** in which there is steric interaction between the adjacent phenyl groups (see *syn*-1,2-diphenyl part in conformer **DR1**). To avoid such severe steric interaction, the intermediate would prefer the *anti*-1,2-phenyl (conformer **DR4**), which would transform to *trans*-2,3-diphenyl-1-benzoylcyclopropane. This, we believe leads to enrichment of *trans*- isomers at the photostationary state.

In an effort to examine the influence of chiral groups during the photoisomerization of benzoylcyclopropane derivatives (which occurs by cleavage of C_1-C_2 *or* C_1-C_3 bond) the chiral perturbers were introduced as an amide or ester linkage at the *meta* and *para* positions of the benzoyl moiety (Scheme 3). Attempts to synthesize the corresponding *ortho* derivatives were unsuccessful. The synthetic procedures and spectroscopic data of *meta* and *para* derivatives of 2,3-diphenyl-1-benzoylcyclopropane are provided in Supporting Information. Irradiation (Pyrex tube) of *cis*-2,3-diphenyl-1-benzoylcyclopropane derivatives in dichloromethane/hexane (0.5 mL/15 mL) solution gave the *trans* isomer with less than 5% diastereomeric excess (de) (Table 1). Similar irradiation in zeolites (loading level 1 molecule per 10 supercages) gave the product *trans* isomer with significant de. Irradiation and analysis protocols are provided in the Experimental Section. The mass balance as estimated with an internal standard (GC analysis) was 95% for all irradiations reported here. However, when the irradiation was conducted for over 1 h, products other than the *trans* isomer were obtained but were not characterized. Perusal of Table 1 reveals that the diastereoselectivities within zeolites are consistently higher than in isotropic solution medium. A given chiral auxiliary brings about higher diastereoselectivity when it is present at the *meta* position than at the *para* position. In general poor diastereoselectivities were obtained within RbY and CsY.

Consistent with the importance of cations on the diastereoselectivity,[5] when the irradiation of *cis*-**1** was carried out within wet NaY zeolite the diastereoselectivity decreased from 71% to 10% (71% A in dry and 10% B in wet NaY), and the de was only 6% when dry silica was used as the medium. In general sample preparation was done within a drybox. Such samples are defined as "dry". These samples in general gave high de. Samples prepared above were saturated with water by keeping them on the pan of a Metler balance. The samples were exposed to moisture till there were no changes in weight. Such samples are defined as "wet" and gave low de. Diastereoselectivity in the case of *cis*-**1** was independent of the duration of irradiation and temperature of the reaction; the de was nearly the same for 5-, 15-, 30-, and 60-min irradiations (70%, 75%, 72%, and 72%). The de at 22 and −58 °C were 71% and 66%.

We first address the site (*meta* vs. *para*)-dependent diastereodifferentiation. The chiral auxiliary functions better at the *meta* than at the *para* position. Depending on the orientation of the amide hydrogen with respect to the amide carbonyl benzoylcyclopropane derivatives *cis*-**1**

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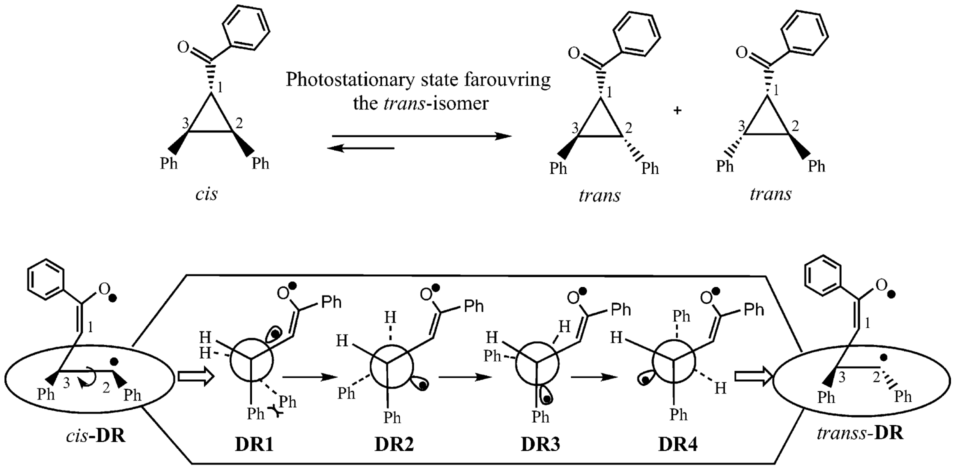
(5) (a) Sivaguru, J.; Natarajan, A.; Kaanumalle, L. S.; Shailaja, J.; Uppili, S.; Joy, A.; Ramamurthy, V. *Acc. Chem. Res.* **2003**, *36*, 509−521. (b) Sivaguru, J.; Shailaja, J.; Uppili, S.; Ponchot, K.; Joy, A.; Arunkumar, N.; Ramamurthy, V. In *Organic Solid State Reactions*; Toda, F., Ed.; Kluwer Academic Press: Dordrecht, The Netherlands, 2002; pp 159−188. (c) Joy, A.; Ramamurthy, V. *Chem. Eur. J.* **2000**, *6*, 1287−1293.

SCHEME 5

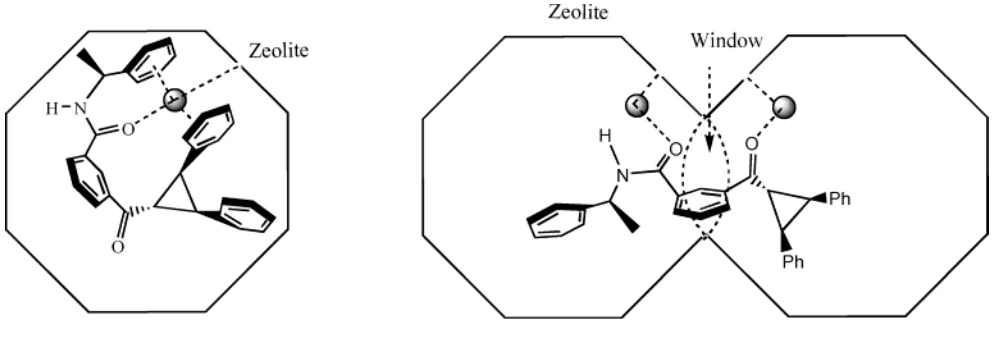


The β-cleavage of the C_1-C_3 bond would also lead similar interaction between the phenyl group

TABLE 1. Diastereomeric Excess in MY Zeolites

substrate	substitution position	% diastereoselectivity in the *trans*-isomer[a] solution	Li	Na	K	Rb	Cs
cis-1	*meta*-derivative	0	8 (A)	71 (A)	14 (A)	5 (A)	3 (A)
cis-3	*para*-derivative	2 (A)	0	11 (A)	1 (A)	0	2 (A)
cis-5	*meta*-derivative	1 (A)	18 (A)	30 (A)	14 (A)	11 (A)	3 (A)
cis-7	*para*-derivative	2 (A)	3 (A)	4 (A)	3 (A)	1 (A)	3 (A)
cis-9	*meta*-derivative	4 (A)	27 (A)	41 (A)	29 (A)	25 (A)	0
cis-11	*para*-derivative	1 (A)	7 (A)	2 (A)	5 (A)	2 (A)	5 (A)
cis-13	*meta*-derivative	3 (A)	20 (A)	38 (A)	15 (A)	12 (A)	1 (A)
cis-15	*para*-derivative	1 (A)	3 (A)	15 (A)	7 (A)	0	0
cis-17	*meta*-derivative	0	15 (B)	25 (B)	52 (B)	13 (B)	4 (B)
cis-19	*para*-derivative	0	1 (A)	1 (A)	11 (A)	1 (A)	0
cis-21	*meta*-derivative	0	1 (A)	11 (A)	14 (A)	5 (A)	8 (A)
cis-23	*para*-derivative	0	0	3 (A)	6 (A)	5 (A)	6 (A)
cis-25	*meta*-derivative	1 (A)	0	2 (A)	7 (A)	0	0
cis-27	*para*-derivative	2 (A)	1 (A)	1 (A)	0	0	0

[a] Peak A and B refers to the first and second peak of that elutes out in the GC/HPLC column. Peak marked A or B in paranthesis is the one obtained in excess.



Anti-conformer

A

Syn-conformer

B

FIGURE 3. Qualitative representations of cation binding to *cis*-**1** (meta derivative) within the supercage of a Y zeolite: (A) the *anti* conformer (amide carbonyl and N−H are *anti*); (B) the *syn* conformer (amide carbonyl and N−H are *syn*).

and *cis*-**3** would exist in *syn* and *anti* conformations (Figures 3 and 4).[6] ^{1}H NMR spectra of *cis*-**1** in solution at room temperature showed a doublet and a quintet for the α-methyl and benzylic hydrogens of the chiral auxiliary, suggesting that the *syn* and *anti* conformers are in equilibrium on the NMR time scale.

We do not know whether the same equilibrium is maintained or a single conformer is preferred within a zeolite. As illustrated in a cartoon representation (Figure 3A), only the *anti* conformer of *cis*-**1** is expected to snugly fit within a supercage. The molecule in the *syn* conformation with an extended geometry (Figure 3B) would most likely fit between two supercages, and in this arrangement the chiral auxiliary would be far away to have influence on the isomerization process. Higher diastereoselectivity within NaY as compared to LiY and KY

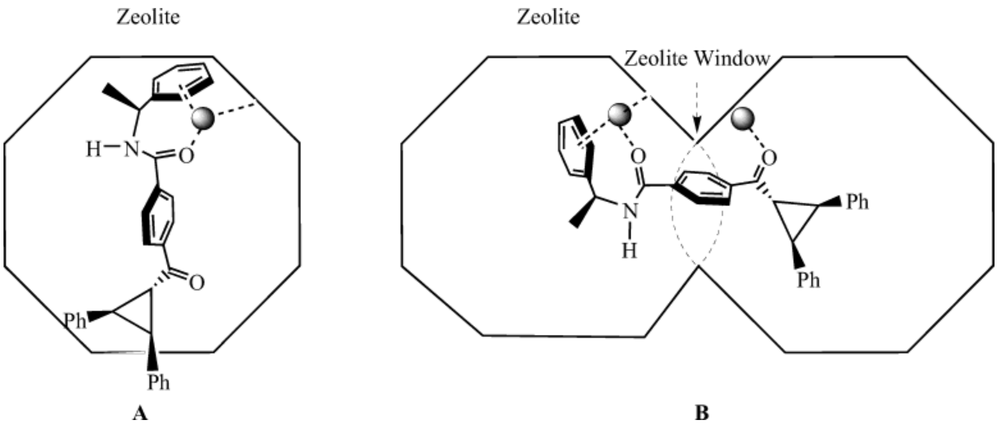


FIGURE 4. Qualitative representations of cation binding to *cis*-**3** (*para* derivative) within the supercage of a Y zeolite: (A) the *anti* conformer within a single supercage; (B) the *anti* conformer between two supercages.

zeolites might be due to a combination of "tight fit"[7] and maximum "cooperative interaction"[8−10] between the cation, chiral auxiliary, and the reaction site. In the examples provided in Table 1 diasteroselectivity within RbY and CsY is small. These large cations probably do not leave enough room for the *meta* derivatives to adopt the *anti* conformation. As shown in Figure 4, substitution at the *para* position probably forces the molecule (*anti* conformer) to spread between two supercages. In this arrangement the interaction between the chiral auxiliary and the reaction site is expected to be small. Observed low diastereoselectivity with *para* isomers is consistent with this qualitative model.

To gain an insight into the cation controlled diastereoselectivity, ab initio and density functional theory calculations were carried out on *cis*-**1** and *cis*-**3**.[11] We utilize the results of gas-phase computations (RB3LYP/6-31G*) to understand the behavior within a zeolite. While one may question the value of gas-phase computational data in understanding the chemical behavior of molecules within a zeolite, a much more complex environment,[12] we find them useful as a guide in building a preliminary model. The most stable Li^+−*cis*-**1** and Li^+−*cis*-**3** structures are shown in Figures 5 and 6. Binding affinities of Li^+ and Na^+ ions to *cis*-**1** and *cis*-**3** are fairly high. The most striking result is that in the case of *meta* derivative (*anti* conformation) the alkali ion interacts with the chiral auxiliary as well as with one of the two phenyls of the diphenylcyclopropane (Figure 5). In this structure (*anti* conformation) the chiral auxiliary is brought closer to the reaction site by the alkali ion. In the *syn* conformation the cation binds only to the amide carbonyl and adopts a linear conformation that is larger than the supercage dimensions. In this structure the chiral auxiliary is not close to the reaction site. Therefore the *syn* conformation is not likely to be important during diastereoselective photoisomerization within zeolites. As shown in Figure 6, in the case of the *para* isomer the cation-bound structure (*anti* conformation) is much longer (18.0 Å) than the width of a supercage.[12] Importantly, in this structure the cation binds only to the chiral auxiliary and the reaction site is far from the chiral auxiliary. Therefore one would expect that the influence of a chiral auxiliary on the isomerization in *para* derivatives to be smaller than in corresponding *meta* derivatives. Experimental results are consistent with this expectation (Table 1). In summary, photoisomerization of 2,3-diphenyl-1-benzoylcyclopropane derivatives provided an opportunity to place the chiral perturber at two positions on the benzoyl part (*para* and *meta*), opening up opportunities to examine the distance dependence of diastereoselectivity. Clearly, in this system the closer the chiral auxiliary to the reaction site the more effective it is.

As per the results obtained with optically pure *trans*-2,3-diphenyl-1-benzoyl-cyclopropane, the triplet diradicals resulting from cleavage of $C_1−C_2$ or $C_1−C_3$ bonds do not equilibrate prior to ring closure (Scheme 4). Since the photoisomerization occurs from the triplet state zwitterionic intermediates are not likely to be important both in solution and within zeolites. The stereodifferentiation must occur at the cleavage (and/or reclosure) stage ($C_1−C_2$ vs $C_1−C_3$), i.e., the rates of the two cleavages (and/or reclosure) in the excited state must be different. In solution, even in the presence of a chiral auxiliary, the two rates appear to be nearly the same (de 5%). On the other hand, α-methyl benzyl amide present at the *meta* position is able to significantly influence the rates of $C_1−C_2$ and $C_1−C_3$ cleavages (and closure) (de 71%). In Figure 5 two structures for Li^+-bound *cis*-**1** are shown. Nature of binding is the same in both cases: the alkali ion binds to the amide carbonyl, phenyl group of the chiral auxil-

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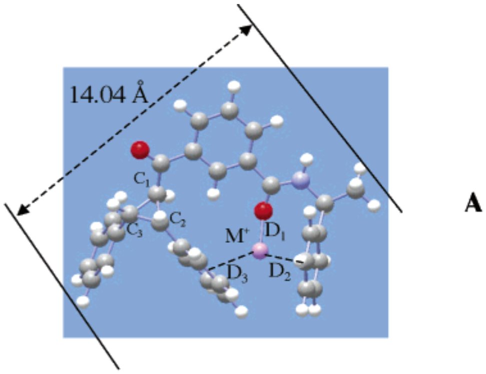
[12] (a) Breck, D. W. *Zeolite Molecular Sieves, Structure, Chemistry and Use*; John Wiley & Sons: New York, 1974. (b) Dyer, A. *An Introduction to Zeolite Molecular Sieves***;** John Wiley & Sons: New York, 1988.

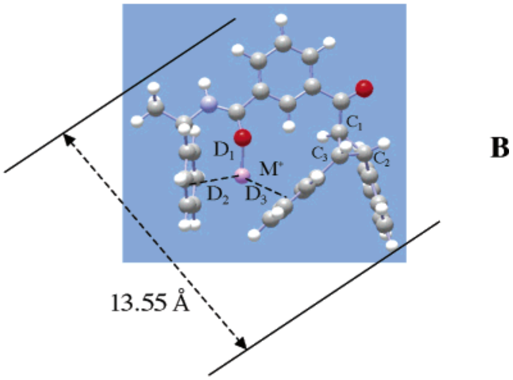
Structural details of M^+ bound to C_2-Phenyl ring on the cyclopropane and to the phenyl ring on the chiral auxiliary



Cation	Binding energy (kcal/mol)	D_1 (Å)	D_2 (Å)	D_3 (Å)	M^+-O-C Angle	Dihedral Angle[a]	
						C_1–C_2/ C=O	C_1–C_3/ C=O
Li^+	86.15	1.81	2.67	2.38	141.67	-86.35	-15.41
Na^+	66.26	2.18	2.71	2.67	137.96	-80.53	-9.90

a) Dihedral angle between the carbonyl attached to the cyclopropane ring and the β-bond on he cyclopropane ring with respect to the carbonyl group.

Structural details of M^+ bound to C_3-Phenyl ring on the cyclopropane and to the phenyl ring on the chiral auxiliary



Cation	Binding energy (kcal/mol)	D_1 (Å)	D_2 (Å)	D_3 (Å)	M^+-O-C Angle	Dihedral Angle[a]	
						C_1–C_2/ C=O	C_1–C_3/ C=O
Li^+	86.65	1.80	2.70	2.35	146.65	15.72	89.79
Na^+	66.82	2.17	2.71	2.67	142.62	12.23	83.28

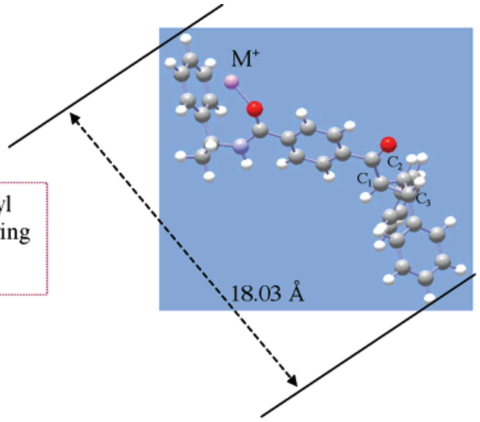
a) Dihedral angle between the carbonyl attached to the cyclopropane ring and the β-bond on he cyclopropane ring with respect to the carbonyl group.

FIGURE 5. Structural parameters and binding energies of Li^+ and Na^+ bound to *anti* conformer of *cis*-**1** computed at RB3LYP/6-31G* level of theory. Structure A: cation bound to C_2-phenyl. Structure B: cation bound to C_3-phenyl.

iary and one phenyl group of the 2,3-diphenyl-cyclopropane. The only difference between the two structures is that in **A** C_2-phenyl interacts with Li^+ and in **B** C_3-phenyl interacts with Li^+. According to computation both structures (**A** and **B**) are equally stable and it is not the difference in energy between the two structures that is responsible for the diastereoselectivity. At this stage we can only speculate. Maybe steric hindrance offered by the zeolite wall is different for the two rotations or one of the two structures is preferred within the zeolite. It is not clear whether the small difference in size between **A** and **B** (Figure 5) would be significant enough for one of them to be preferred within a zeolite. We admit that at this stage we are unable to offer a convincing rationale for the observed interesting results.

The examples presented above demonstrate convincingly that the confined space of a zeolite could serve as a useful medium to achieve asymmetric induction during a photoreaction. Consistently higher de has been obtained within zeolites than in solution.[5] The confined space and the cations are believed to be responsible for the observed asymmetric induction within zeolites. The effectiveness of a chiral auxiliary in benzoylcyclopropane derivatives depends on the site of its attachment to the benzoyl ring. The most likely factor responsible for the high selectivity could be a combination of the conformational preference and tightness of fit within the supercages of a zeolite. With several independent examples we have shown that the method described here for *cis*-2,3-diphenyl-1-benzoylcyclopropane derivatives is fairly general. In the current study the highest de obtained is 71% in NaY zeolite with α-methyl benzylamine as the chiral auxiliary. Extensive studies carried out with *cis*-2,3-diphenylcyclopropane-1-carboxylic acid derivatives revealed that α-methyl ben-

Structural details of M$^+$ bound to C$_2$-Phenyl ring on the cyclopropane and to the phenyl ring on the chiral auxiliary



Cation	Binding Affinity (kcal/mol)	C=O---M$^+$ (Å)	Benzene^a---M$^+$ (Å)	M$^+$-O-C Angle	Dihedral Angle^b	
					C$_1$–C$_2$/ C=O	C$_1$–C$_3$/ C=O
Li$^+$	78.19	1.80	2.01	135.00	-47.82	19.53
Na$^+$	57.42	2.14	2.47	139.13	-47.16	20.18

a) Benzene ring on the chiral auxiliary.

b) Dihedral angle between the carbonyl attached to the cyclopropane ring and the β-bond on he cyclopropane ring with respect to the carbonyl group.

FIGURE 6. Structural parameters and binding energies of Li$^+$ and Na$^+$ bound to *anti* conformer of *cis*-**3** computed at the RB3LYP/6-31G* level of theory.

zylamine is an excellent chiral auxiliary in this system as well. During direct excitation 80% de was obtained in LiY and 75% de during triplet-sensitized isomerization to the corresponding *trans* isomer.[1] Currently, we are unable to provide a simple model that can predict the outcome of asymmetric induction within zeolites. Further work is underway to reach this goal.

Experimental Section

Monovalent cation-exchanged zeolites (LiY, KY, RbY, and CsY) were prepared by refluxing 10 g of NaY with 100 mL of a 10% solution of the corresponding metal nitrate in water for 24 h. The exchanged zeolite was filtered and washed thoroughly with distilled water. This procedure was repeated three times. Subsequently, the cation-exchanged zeolite was dried at 120 °C for about 3 h and stored. All solvents were used as purchased. THF was dried over sodium/benzophenone under nitrogen prior to use. Deionized water was used when needed. All chiral auxiliaries used as alcohols or amines during synthesis were commercial samples. *cis*-2,3-Diphenylcyclopropane-1-carboxylic acid and *trans*-2,3-diphenylcyclopropane-1-carboxylic acid were prepared by literature procedure.[13]

Photoisomerization of *cis*-2,3-Diphenyl-1-benzoyl-cyclopropane and Pure Isomer of *trans*-2,3-Diphenyl-1-benzoyl-cyclopropane in Solution. Direct Irradiation. The compound (*cis* or pure isomer of *trans*) was dissolved in 0.5 mL of dichloromethane in a test tube followed by the addition of 15 mL of hexane. The test tube was stoppered with a rubber septum and wound with parafilm. The solution was degassed with N$_2$ for 30 min and irradiated (unfiltered output from a 450-W medium-pressure mercury lamp) for different time intervals. The solution was concentrated and analyzed by HPLC.

Photoisomerization of Pure Isomer of *trans*-2,3-Diphenyl-1-benzoyl-cyclopropane inside Zeolites. The pure stereoisomer (RR or SS isomer) of *trans*-2,3-diphenyl-1-benzoyl-cyclopropane (2−3 mg) was dissolved in 0.5 mL of dichloromethane in a test tube, and 15 mL of hexane was added to the test tube and stirred. MY (M = Li$^+$, Na$^+$, K$^+$, Rb$^+$, and Cs$^+$) zeolite (~300 mg) activated at 500 °C was added with stirring. The test tube was stoppered with rubber septum, wound with Parafilm, and stirred for 8 h. The zeolite complexwas deaerated with nitrogen for 30 min and then irradiated (unfiltered output from a medium pressure of Hg lamp) as a hexane slurry and filtered. Analysis of the hexane supernatant after irradiation did not show the presence of reactant/photoproducts. The reactant and the photoproducts were extracted from the zeolite by stirring with acetonitrile for 8−10 h. The acetonitrile extract was concentrated and analyzed on HPLC. HPLC conditions (chiral stationary phase): column AD-RH; eluent hexane/2-propanol = 95:05; monitoring wavelength 274 nm; flow 0.5 mL/min; retention time *cis* ~11.1 min, *trans*-SS-isomer ~30.5 min; *trans*-RR-isomer ~36.5 min.

Photoisomerization of Chiral Amides and Esthers in Solution. *cis*-2,3-Diphenyl-1-benzoylcyclopropane derivative (2−3 mg) was dissolved in 0.5 mL of dichloromethane in a test tube followed by the addition of 15 mL of hexane. The test tube was stoppered with a rubber septum, wound with parafilm, and bubbled with N$_2$ for 30 min. The solution was irradiated (unfiltered output from a 450-W medium-pressure mercury lamp) for 10−15 min under positive N$_2$ pressure, concentrated, and analyzed by GC/HPLC.

Photoisomerization of Chiral Amides Esthers within Zeolites. Activated MY zeolite (~300 mg; M = Li$^+$, Na$^+$, K$^+$, Rb$^+$, and Cs$^+$) was added to a stirred solution of the benzoylcyclopropane derivative (3−5 mg; one molecule per 12 supercages) dissolved in 0.5 mL of dichloromethane and 15 mL of hexane in a test tube. The test tube was stoppered with a rubber septum, wound with parafilm, and stirred for 8 h in a

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[13] (a) Blatchford, J. K.; Orchin, M. *J. Org. Chem.* **1964**, *29*, 839. (b) D'Yakanov, I. A.; Komendantev, M. I.; Gui, F.-S.; Korichev, G. L. *J. Gen. Chem. USSR* **1962**, *32*, 928. (c) Applequist, D. E.; Gdanski, R. D. *J. Org. Chem.* **1981**, *46*, 2502. (d) Inoue, Y.; Yamasaki, N.; Shimoyama, H.; Tai, A. *J. Org. Chem.* **1993**, *58*, 1785−1793.

water bath kept at 55 °C. The slurry was filtered and washed with hexane. Analysis of the filtrate (hexane solution) by HPLC/GC indicated that benzoylcyclopropane derivative was completely incorporated within the zeolite. The zeolite/substrate complex was dried under vacuum (2×10^{-3} Torr) with heating at 60 °C. The moisture free zeolite complex was transferred to a test tube inside a drybox, and then 15 mL of fresh dry hexane was added to the test tube. The test tube was stoppered with a rubber septum and wound with parafilm. The zeolite complex was purged with nitrogen (20 min), irradiated (unfiltered output from a medium pressure of Hg lamp) as hexane slurry under positive nitrogen pressure for 10−15 min, and filtered. Analysis of the hexane supernatant after irradiation did notshow the presence of reactant/photoproducts. The reactant and the photoproducts were extracted from the zeolite by stirring with acetonitrile for 8−10 h in a water bath kept at 55 °C. The acetonitrile extract was concentrated and analyzed on GC/HPLC.

Analysis Conditions. The analysis conditions for the compound (**1**−**28**) are given in Table 1 of Supporting Information.

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Supporting Information Available: Synthetic procedures and structural data of reactants and products **1**−**28**, synthesis of *cis* and *trans* isomers of 2,3-diphenyl-1-benzoylcyclopropane and determination of absolute configuration of *trans*-2,3-diphenyl-1-benzoylcyclopropane, and compilation of Cartesian coordinates and total energies for computed structures related to Figures 5 and 6. This material is available free of charge via the Internet at http://pubs.acs.org.

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