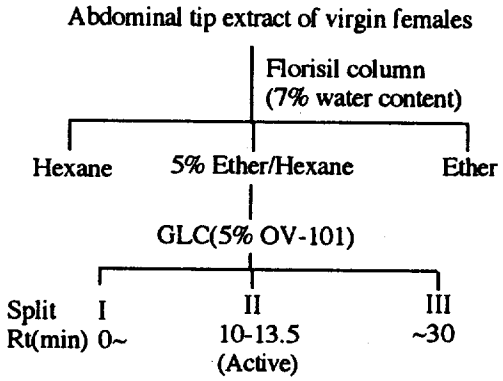


Figure 1. Purification of the extract of the sex pheromone.

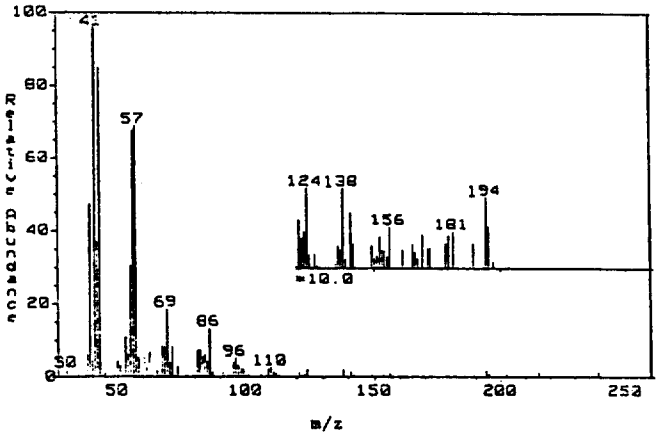
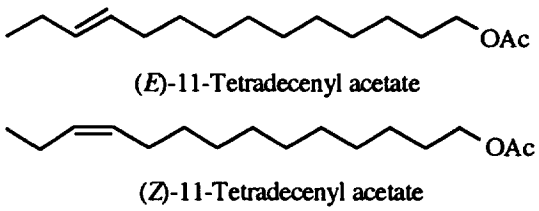


Figure 2. GC-MS of the biologically active fraction of the female extract.



(*E*)-11-Tetradecenyl acetate

(*Z*)-11-Tetradecenyl acetate

Figure 3. The isomers of 11-tetradecenyl acetate.

method of DIP/MS (EI) programmed from room temperature to 400 ℃ at 32 ℃/min. The active fraction which had retention time of ~10.3 min showed two mass spectra of M^+-60 peak at m/z 194 indicating two structures of 11-tetradecenyl acetate isomers (Figure 2). Important fragmentations indicating then presence of double bond at C_{11}-C_{12} bond were observed at m/z 69 ($CH_3CH_2CH{=}CHCH_2^+$) resulting from allylic cleavage, at m/z 70 ($CH_2{=}CHCH_2CH_2CH_3^+$) arising from McLafferty rearrangement, and an interval of 14 amu was observed between the most intense peaks of clusters of fragments. Also, we have observed between the most intense peaks of clusters of fragments. Also, we have observed m/z 61 by "double H-transfer" and m/z 41 ($C_3H_5^+$, base peak), 55 ($C_4H_7^+$), 69 ($C_5H_9^+$) and resonance stabilized peak at m/z 43 (CH_3CO^+). These ion peaks of the compounds identified were compared with the mass spectra of the synthesized (*E*)-and (*Z*)-11-tetradecenyl acetate.[4,5]

Micro-ozonolysis of both compounds yielded 11-acetoxyundecenal, which was also confirmed by GC-MS.

From the above data, (*E*)-and (*Z*)-11-tetradecenyl acetates (Figure 3) were identified as two components of the sex pheromone compounds of the perilla leaf pyralid moth.

Field test and determination of the ratio of (*Z*)-and (*E*)-forms will be the subject of our future research.

Acknowledgment. This work was supported by NON DIRECTED RESEARCH FUND, Korea Research Foundation, 1993.

References

1. Seol, K.-Y.; Goh, H.-G. *Korean J. Appl. Entomol.* **1990**, *29*, 190.
2. Carrol, K. K. *J. Lipid Res.* **1961**, *2*, 135.
3. Recently, we have reported the EAG responce of the diamond back moth. See: Kang, S. K.; Seol, K.-Y.; Jun, J.-G.; Goh, H.-G.; Kim, J.-J. *J. Korean Chem. Soc.* **1990**, *34*, 179.
4. The synthetic (*E*)-and (*Z*)-11-tetradecenyl acetates were synthesized by our procedure: Kang, S.-K.; Ku, M.-S.; No, K.; Lee, J.-O. *J. Korean Chem. Soc.* **1987**, *31*, 576.
5. The GC-MS data of (*E*)-and (*Z*)-11-tetradecenyl acetate was provided by Professor T. Ando, The University of Tokyo.

Irreversible Cis-trans Photoisomerization of 1,2-Dibenzoyl-3-Phenylcyclopropane

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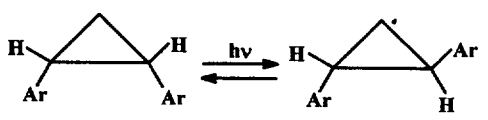
In the early papers of Hammond[1] and Griffin,[2] photochemical *cis-trans* isomerization of 1,2-dibenzoylcyclopropane was investigated. Irradiation of *cis*-1,2-dibenzoylcyclopropane affords trans isomer, and the reaction was shown to be reversible. In this isomerization, maximum stabilization of the diradical would be achieved by cleavage of the bond beta to both carbonyl groups.

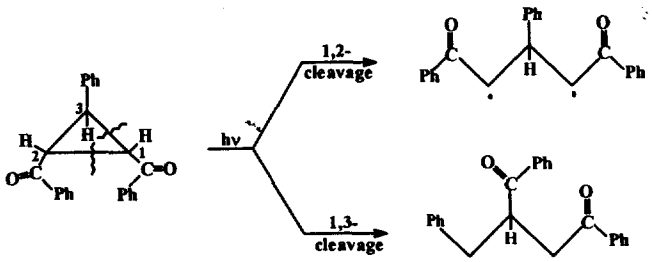
A similar photoisomerization *cis*-1-benzoyl-2-phenylcyclopropane to trans isomer has been observed[3] (eq. 1).



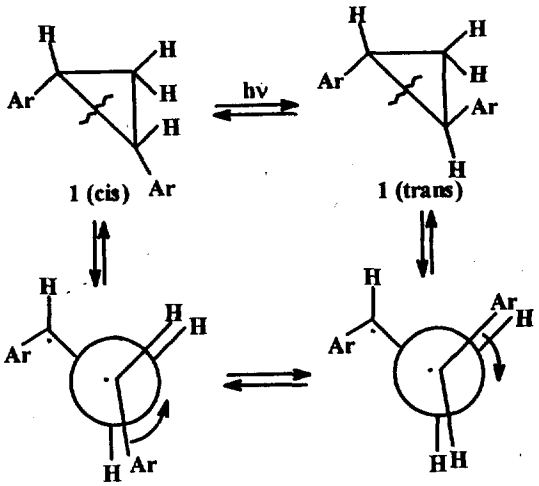
1 (cis) **1 (trans)**

Ar = Ph, COPh

(1)



Scheme 1.

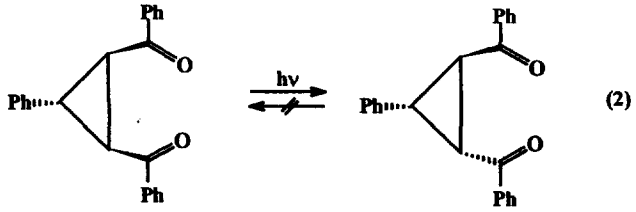


Scheme 2.

In 1,2-dibenzoyl-3-phenylcyclopropane,[4~6] however, the bond cleavage could occur in two different ways which might affect reversibility of *cis-trans* isomerization (Scheme 1).

Herein we wish to report photochemical reaction of 1, 2-dibenzoyl-3-phenylcyclopropane (2) analyzing the conformations of diradical which is concerned to reversibility of *cis-trans* isomerization.

Irradiation of *cis*-1,2-dibenzoyl-3-phenylcyclopropane in ether at 300 nm affords trans isomer and the isomerization is shown to be irreversible, as irradiation of trans isomer does not give *cis* isomer (eq. 2).

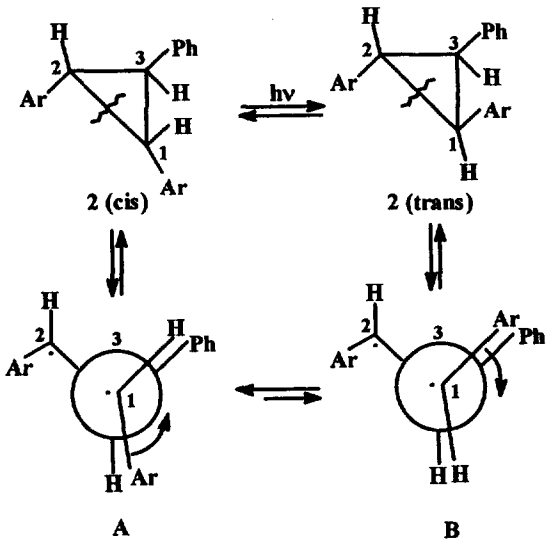


(2)

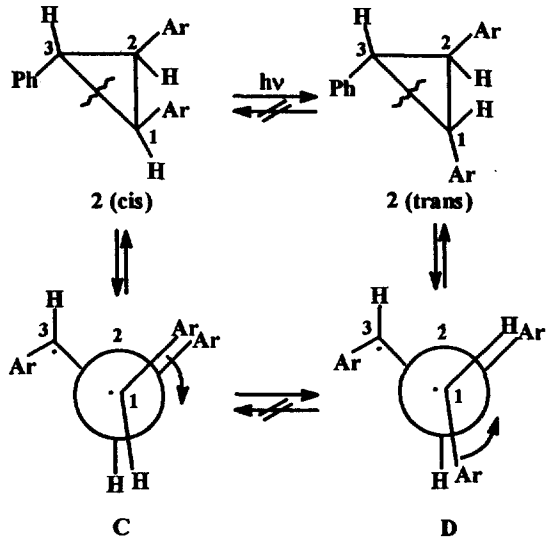
Quantum efficiency for the isomerization is 0.26 in both disappearance of *cis*-2 and appearance of trans-2, which means that the isomerization is quantitative.

Cis-trans photoisomerization of 1 is reversible, while the isomerization of *cis*-2 is irreversible. The reversible isomerization of 1 can be explained by the same rotational energy barriers between two conformers of diradical intermediates (Scheme 2).

In photoisomerization of *cis*-2, the bond cleavage could occur in two different ways (Scheme 1). 1,2-Bond cleavage leads to an intermediate conformer A (Scheme 3), while 1,3-bond cleavege leads to an intermediate conformer C (Scheme 4).



Scheme 3.



Scheme 4.

In 1,2-Bond cleavage of *cis*-2, conversion of an intermediate conformer A to B is unfavorable while the reverse process is favorable comparing rotational energy barriers of the conformer A and B (Scheme 3).

Considering rotational energy barriers of the conformers A and B, irradiation of trans-2 should give *cis* isomer. Since this is not the case for the experimental results, 1,2-bond cleavage for the isomerization of 2 is eliminated.

In 1,3-bond cleavage of *cis*-2, conversion of an intermediate conformer C to D is favorable process while the reverse process is unfavorable comparing rotational energy barriers of the conformers C and D (Scheme 4).

Since these conformational analyses of the conformers C and D are coincident to the experimental results, we concluded that 1,3-bond cleavage of *cis*-2 is responsible for the

irreversible *cis-trans* isomerization of 2.

The photoreduction of 1 in hydrogen donor solvents takes a completely different course in the presence of photosensitizers such as benzophenone. Under these conditions, the primary reaction is reduction to 1,3-dibenzoylpropane.[3]

Radical trapping experiment and C-3 methyl substituent effect are under investigation to obtain further information on the arguments in 1,2- *vs.* 1,3-bond cleavage of 1,2-dibenzoyl-3-phenylcyclopropane.

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References

1. Hammond, H. A.; O'Connel, E. J.; Griffin, G. W. *J. Amer. Chem. Soc.* **1963**, *85*, 1001.
2. Griffin, G. W.; Petterson, R. C.; Dodson, R. M. *J. Amer. Chem. Soc.* **1965**, *87*, 1410.
3. Champman, O. L. *Organic Photochemistry*; Marcel Dekker, Inc.: New York, U.S.A., 1967, vol. 1, p 116.
4. Chapdelaine, M. J.; Hulce, M. *Org. React.* **1990**, *38*, 225.
5. Helmquist, P. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, U.S. A., 1991; vol. 4, p 986 and references cited therein.
6. Greenberg, F. H.; Schulman, E. M. *J. Org. Chem.* **1993**, *58*, 5853.

B-t-Butoxydiisopinocampheylborane as a Highly Chemoselective Reducing Agent for Aldehydes

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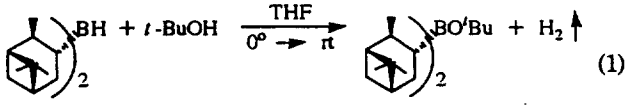
Very recently, we reported that *B*-hydroxydiisopinocampheylborane (Ipc_2BOH),[1] a newly synthesized reagent, is an exceptionally mild, highly selective reducing agent for the reduction of only the aldehyde group in the presence of keto and all other functional groups. The reagent has proven to be superior to all of eariler reagents.[2] In continuation of our efforts to explore new reducing systems for such transformations, we prepared a series of *B*-alkoxydiisopinocampheylborane (Ipc_2BOR) and examined the reducing action toward general organic functional groups. In the course of this systematic study, we found that *B-t*-butoxydiisopinocampheylborane (Ipc_2BO^tBu) reduces only the aldehydes cleanly, while all common organic functional groups are not affected. Herein, we report the results for such selective reduction of aldehydes by Ipc_2BO^tBu in pentane.

The reagent can be readily prepared by alcoholysis of diisopinocampheylborane (Ipc_2BH)[3] in THF solution (Eq. 1). After the complete evolution of hydrogen, the solvent was distilled out under reduced pressure and replaced with pentane.



(1)

Ipc_2BH Ipc_2BO^tBu

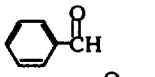
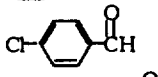
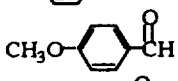
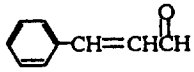
Ipc_2BO^tBu is an effective reagent for the reduction of a wide variety of aldehydes in pentane at 25°. Lke the case of Ipc_2BCl[3] and Ipc_2BOH,[1] the formation of an intermediate alkoxyborane is accompanied by the elimination of α-pinene. The treatment of the reaction mixture with acetaldehyde (liberation of the second α-pinene) followed by addition of aqueous sodium hydroxide affords the alcohol product.[4]

The transformation of representative aldehydes to the corresponding alcohol with 10% excess reagent at 25° in pentane is listed in Table 1. A wide variety of aldehydes are reduced completely in less than 6 h. α,β-Unsaturated aldehydes are also reduced to the corresponding allylic alcohols cleanly.

The chemoselectivity of this reagent was tested with several representative aldehyde-ketone pairs and aldehyde-other reactive compound pairs in competition experiments. Equimolar amounts of two compounds were allowed to compete for a limited quantity of Ipc_2BO^tBu (1 equivalent). A standard solution of the reagent (*ca.* 2 M) in pentane maintained at 25°.

After 6 h, the mixture was treated with acetaldehyde and hydrolyzed with aqueous sodium hydroxide. The results ob-

Table 1. Reduction of Aldehydes to Alcohols with Ipc_2O^tBu in Pentane at 25°[a]

Substrate	Time (h)	Yields (%)[b]
$CH_3(CH_2)_2CH$	1	100
$CH_3(CH_2)_4CH$	3	100
	3	100
	3	100
	3	100
$CH_3CH{=}CHCH$	3	100
$CH_3(CH_2)_2CH{=}CHCH$	6	100
	12	100

[a]Ten % excess reagent was utilized. Reaction mixtures were *ca.* 1 M in substrates. [b]Yields of the corresponding alcohols determined by GLC using appropriate internal standard.