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A Novel and Selective Photoisomerization of Allylic Benzoates

Tao Hu and E. J. Corey*

Department of Chemistry and Chemical Biology Harvard University, 12 Oxford Street,
Cambridge, Massachusetts 02138

corey@chemistry.harvard.edu

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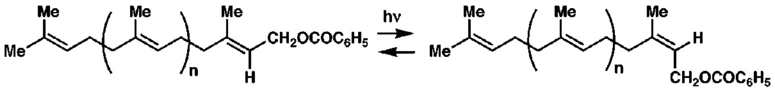
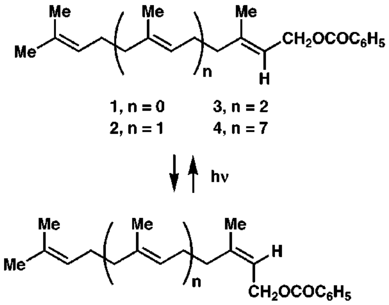
ABSTRACT



Ultraviolet irradiation of a series of polyunsaturated allylic benzoates results in highly selective *E*/*Z* interconversion of the allylic double bond.

We describe herein an interesting and, to the best of our knowledge, novel photoisomerization of the ethylenic linkage in benzoate esters of allylic alcohols. For example, irradiation of (*E*)-geranyl benzoate (**1**) in a methylcyclohexane solution (0.01−0.04 M under Ar or N_2; UV max, 227, 273, 280 nm; ϵ, 7270, 600, 500) at 0 °C using a medium pressure mercury vapor lamp in a Penn-Orr microreactor[1] (available from Ace Glass Co.) resulted in photoequilibration of the 2,3-ethylenic linkage in 1−2 h with formation of a mixture of *E*- and *Z*-isomers in a ratio of 41:59. The reaction was extremely clean since no other products could be detected by careful thin layer chromatographic and 500 MHz ^{1}H NMR analysis. Similarly, irradiation of 2,6-(*E*,*E*)-farnesyl benzoate (**2**) for 40 min under the same conditions afforded cleanly a 55:45 mixture of 2(*E*),6(*E*)- and 2(*Z*),6(*E*)-farnesyl benzoates by selective stereomutation of the allylic olefinic linkage. Under the same conditions 2,6,10-(*E*,*E*,*E*)-geranylgeranyl benzoate (**3**) was transformed cleanly in 40 min to a 48:52 mixture of 2,6,10-(*E*,*E*,*E*)- and 2,6,10-(*Z*,*E*,*E*)-geranylgeranyl benzoates. Finally, irradiation of (*all-E*)-nonaprenyl (solanasyl) benzoate (**4**) for 40 min under identical conditions resulted in clean and highly selective photoisomerization of the 2*E*-olefinic linkage to form a mixture of 2*E*- and 2*Z*-isomers in a ratio of 48:52. Under these conditions, the more remote ethylenic linkages in **2**, **3**, and **4** did not undergo detectable *E*/*Z* photointerconversion.



1, n = 0 **3**, n = 2
2, n = 1 **4**, n = 7

2*E*- + 2*Z*- **1** - **4**

Irradiation of (*E*)-geranyl 4-methoxybenzoate also resulted in *E*/*Z* equilibration of the 2,3-olefinic linkage (*E*/*Z* ratio 45:55 after 20 min and 42:58 after 40 min) as did irradiation of (*E*)-geranyl 3-methoxybenzoate (*E*/*Z* ratio 74:26 after 20 min, 67:33 after 40 min and 62:38 after 70 min). In contrast, irradiation of either (*E*)-geranyl 2-, 3-, or 4-nitrobenzoate for 3.5 h under the same conditions led to no detectable isomerization of the 2-olefinic linkage or other reaction as determined by TLC and 500 MHz ^{1}H NMR analysis.

We have also studied the photoisomerization reaction with the 4-methoxybenzoate esters of (*E*)- and (*Z*)-2-octen-1-ol (**5** and **6**, respectively). Irradiation of these esters in a 0.02 M solution in methylcyclohexane at 0 °C under Ar led cleanly to the same 74:26 *E*/*Z* mixture of **5** and **6** after either 20 or 40 min. This photoisomerization was also carried out under an atmosphere of O_2 with no significant change in the reaction as compared with that for an Ar atmosphere. Indeed, it was also observed that the photoisomerizations of substrates **1**−**4** as described above proceeded just as well under O_2 as with an Ar atmosphere. As a further example, we investigated the irradation of the *E*,*Z*-triene benzoate **7**.

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[1] Penn, J. H.; Orr, R. D. *J. Chem. Educ.* **1989**, *66*, 86.

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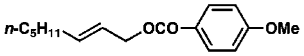
Under the standard conditions which were applied for the photoisomerizations of **1**−**6**, benzoate **7** underwent clean *Z*/*E* isomerization selectively at the 6-olefinic linkage of the allylic benzoate subunit. The *Z*/*E* ratios were found to be 30:1 (initial composition) at zero time, 60:40 after 12 min, 46:54 after 30 min, and 44:56 after 55 min of irradiation.



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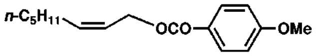

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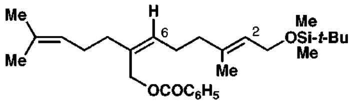

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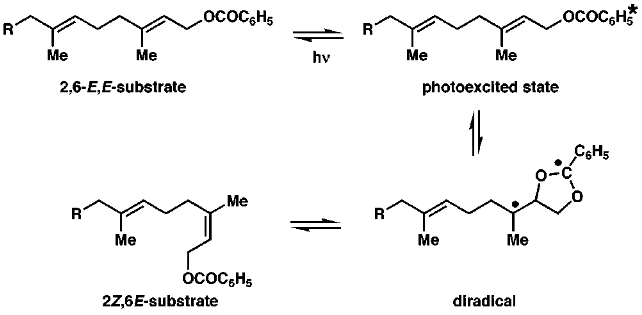
The exploratory studies described herein have revealed an interesting new aspect of the photoisomerization of ethylenic linkages. In the absence of extensive physical investigations, the mechanistic details of these isomerizations must remain a matter of conjecture. However, there would appear to be two broad types of processes which may be involved. The first is a photophysical mechanism involving electronic excitation of the benzoyl moiety[2] followed by energy transfer to the nearby allylic double bond and subsequent rotation about its σ-axis to effect *E*/*Z* interconversion. Such a process could involve either singlet or triplet electronically excited states. The fact that the photoisomerization of substrates **1**−**6** is not inhibited by an atmosphere of O_2 somewhat favors the involvement of singlet states (Förster energy transfer)[3] rather than intramolecular triplet−triplet energy transfer,[4] although it is certainly not decisive. An alternative photophysical pathway for isomerization involves electron transfer from C═C to the electronically excited benzoyl group to form a radical cation which can undergo facile C−C rotation and electron return.[5] The second type of process is a photochemical mechanism, one version of which is shown in Scheme 1. This reversible photochemical pathway generates a new chemical intermediate, such as the diradical shown in Scheme 1 which can undergo facile rotation about the σ-component of the bond undergoing stereomutation. Clearly, the lifetime of any chemical intermediate must be short compared to its rate of capture by O_2, in view of the lack of any photoreaction of substrates **1**−**6** with O_2 under our standard conditions. There is some precedent for the pathway outlined in Scheme 1 in previously reported photoreactions of methyl benzoate. The most relevant is the [2 + 2]-photoaddition reaction with olefins to form oxetanes[4] which is probably a two-step cycloaddition process via 1,4-diradicals.[6,7]

Scheme 1



Upon prolonged irradiation of farnesyl benzoate (**2**), *E* → *Z* isomerization can be observed not only in the 2-olefinic linkage but also in the 6-olefinic bond. The much slower isomerization about the more remote 6-olefinic bond of **2** would be consistent with either a photochemical pathway such as that shown in Scheme 1 or a photophysical (energy or electron transfer)[3] process, both of which are expected to be slower than for the allylic double bond. The remote isomerization also is clearly intramolecular since it occurs at the same rate at concentrations from 0.02 to 0.002 M.

Because of the facile photoisomerization of allylic benzoates reported above, we have also examined the photochemical stability of farnesyl acetate which shows an apparent absorption max at 238 nm (ϵ = 280) in the methylcyclohexane solution. Irradiation of farnesyl acetate (0.02 M in methylcyclohexane) with the same apparatus as used for the allylic benzoates **1**−**7** resulted in a slow but definite photoisomerization of the 2-ethylenic linkage to give an 88:12 *E*/*Z* mixture after 1 h and an 83:17 *E*/*Z* mixture after 2 h. The low-intensity 238 nm absorption of farnesyl acetate may correspond to an electronic transition which is enhanced by the proximity of acetate and olefinic functions, since it does not appear in the spectrum of ethyl acetate (end absorption only at 238 nm, ϵ ca. 1). In any event that excitation could lead to photoisomerization by any of the paths discussed above.

In summary, we have observed an intriguing new type of stereomutation of nonconjugated olefinic linkages involving photoexcitation of allylic benzoates or other esters. The mechanistic aspects of this reaction invite further studies which could deepen our understanding of organic photochemistry of a little studied class of compounds.

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(2) Ultraviolet absorption of benzoate esters in MeOH at 280 nm (ϵ ~ 1000) excites an $\pi\pi^*$ transition ($^1A_{1g} \rightarrow {}^1B_{2u}$) and that at 230 nm ($\epsilon$ ~ 14 000) excites an intramolecular charge-transfer transition. Either or both of these excitations may be involved in the photochemistry described herein. See: (a) Tanaka, J.; Nagakura, S.; Kobayashi, M. *J. Chem. Phys.* **1956**, *24*, 311. (b) Tanaka, J.; Nagakura, S. *J. Chem. Phys.* **1956**, *24*, 1274. (c) Nagakura, S.; Tanaka, J. *J. Chem. Phys.* **1954**, *22*, 236.

(3) For a discussion, see: Klessinger, M.; Michl, J. *Excited States and Photochemistry of Organic Molecules*; VCH Publications: New York, 1995; pp 291−295.

(4) (a) Cantrell, T. S. *J. Chem. Soc., Chem. Commun.* **1973**, 468. (b) Cantrell, T. S.; Allen, A. C. *J. Org. Chem.* **1989**, *54*, 135.

(5) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401.

(6) See ref 3, pp 424−432.

(7) Another interesting photoreaction of methyl benzoate is the photoaccelerated reduction by sodium borohydride. See: (a) Choi, J. H.; Kim, D. W.; Shim, S. C. *Tetrahedron Lett.* **1986**, *27*, 1157. (b) Wigfield, D. C.; Feiner, S.; Gowland, F. W. *Tetrahedron Lett.* **1976**, 3377. For this reaction Choi et al. report that the quantum yield for reduction of methyl benzoate (0.50) is greater than that for methyl 4-methoxybenzoate (0.03) or methyl 4-nitrobenzoate (0.05).