Pergamon

Tetrahedron Letters 40 (1999) 2335–2338

TETRAHEDRON
LETTERS

Diastereoselective [3+2]-Photocycloaddition of Chiral 1,4-Naphthalenedicarboxylic Esters to Alkenes

Yasuo Kubo,*[1] Masahiro Yoshioka, Satoshi Nakajima, and Isamu Inamura

Department of Materials Science, Faculty of Science and Engineering, Shimane University, Matsue, Shimane 690-8504, Japan

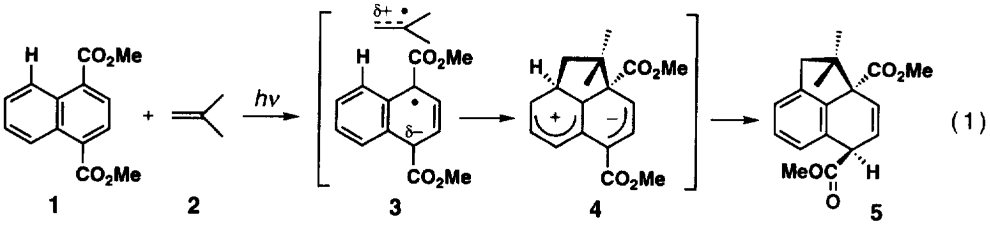
Received 2 December 1998; revised 11 January 1999; accepted 18 January 1999

Abstract: [3+2]-Photocycloaddition of di-(-)-menthyl, di-(-)-8-phenylmenthyl, and di-(-)-bornyl 1,4-naphthalenedicarboxylates to alkenes, such as isobutene, styrene, and α-methylstyrene, proceeded with diastereoselectivity, up to 62% diastereomeric excess (de), largely depending on the concavity of the auxiliary, steric bulk of the substituents of the alkenes, and reaction temperature. The de values remarkably increased with decrease of the reaction temperature, and linear dependence of ln(diastereomeric ratio) on 1/T was observed.

Keywords: photochemistry; diastereoselection; cycloadditions; esters

Photochemical strategies for asymmetric induction have received considerable attention in recent years [1-10], and several types of inter- and intra-molecular photochemical reactions, such as [2+2]-cycloaddition [3], [4+2]-cycloaddition [4], [4+4]-cycloaddition [5], oxetane formation [6], hydrogen abstraction [7], di-π-methane rearrangement [8], photodeconjugation [9], and others [10], have so far been utilized in the asymmetric induction by using chiral auxiliaries. Especially from the synthetic viewpoint, the diastereoselectivity of [2+2]-cycloaddition of enones to alkenes and oxetane formation of ketones with alkenes has been extensively investigated [3,9].

On the other hand, we have found a novel 1,8-photoaddition of dimethyl 1,4-naphthalenedicarboxylate (**1**) to alkenes, such as isobutene (**2**), a formal [3+2]-cycloaddition, which proceeds stereospecifically, possibly from the singlet excited state of **1** via formation of an exciplex **3** and an almost synchronous two-bond formation in **1** to give a zwitterionic intermediate **4** followed by proton transfer (eq 1) [11].



(1)

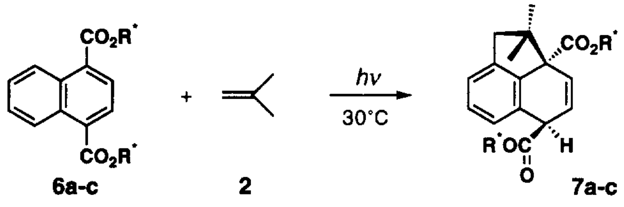
---

[1] E-mail: kubo@riko.shimane-u.ac.jp

PII: S0040-4039(99)00180-X

In this letter, we present our results on diastereoselective [3+2]-photocycloaddition of (-)-menthyl, (-)-8-phenylmenthyl, and (-)-bornyl diesters of 1,4-naphthalenedicarboxylic acid **6a-c** to alkenes as the first example of a diastereoselective [3+2]-photocycloaddition.

Irradiation of an acetonitrile solution of menthyl ester **6a** (2.0×10^{-3} mol/dm^3) and **2** (1.0 mol/dm^3) with a high-pressure Hg lamp through an uranium filter (> 320 nm) under a nitrogen atmosphere at 30°C gave a mixture of two diastereomers of [3+2]-adducts **7a** in a good yield (eq 2, entry 1 in Table 1). The diastereomeric mixture of the adducts **7a** was isolated by column chromatography on silica gel. Their structures were assigned on the basis of their spectral properties, especially of the similarity of the ^{1}H NMR spectrum to that of **5**. The diastereomeric ratio of 1.59, which corresponded to 23% diastereomeric excess (de), could be determined from the ^{13}C NMR spectrum of the isolated mixture with good reproducibility, although an attempt to determine the ratio from the ^{1}H NMR spectrum was unsuccessful due to the serious overlapping of the signals. The diastereomeric ratio was confirmed to remain almost constant during the course of the reaction.



(2)

Table 1

Diastereoselectivity in the [3+2]-photocycloaddition of chiral 1,4-naphthalenedicarboxylic esters **6a-c** to isobutene (**2**).[a]

Entry	Ester	R*	Solvent	Irradiation Time (h)	Yield (%)[b]	Diasteremeric Ratio[c]	de (%)[d]
1	**6a**	Menthyl	MeCN	8	76	1.59	23
2			Et_2O	16	75	1.61	23
3			C_6H_6	32	69	1.55	22
4	**6b**	8-Phenylmenthyl	MeCN	16	43	2.77	47
5	**6c**	Bornyl	MeCN	12	65	1.13	6

a Irradiation conditions are as follows; *hν* through an uranium filter (> 320 nm), under N_2, at 30°C, [**6a-c**] = 2.0×10^{-3} mol/dm^3, [**2**] = 1.0 mol/dm^3.

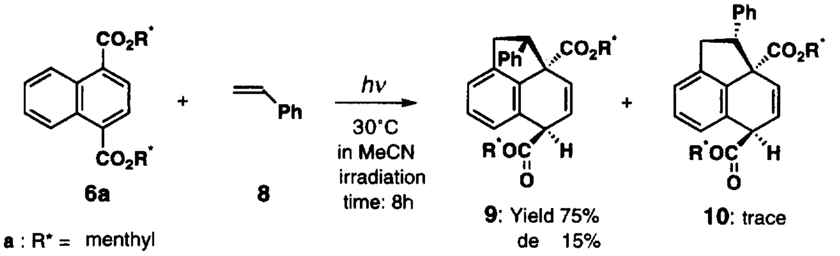
b Total yield of the two diastereomers of **7a-c**.

c Diastereomeric ratio of **7a-c** determined by ^{13}C NMR analysis of the isolated mixture.

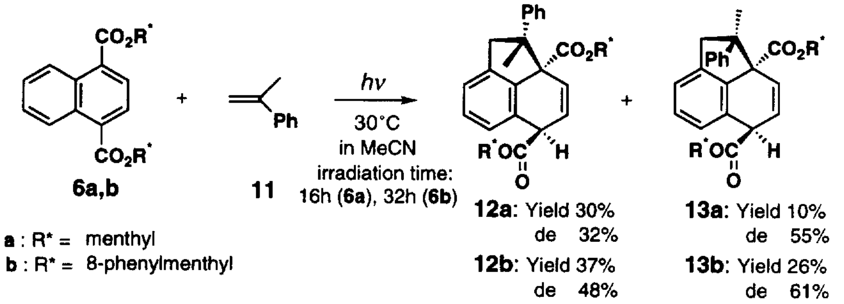
d Diastereomeric excess determined by de = (I - I') / (I + I'), where I and I' are the intensity of the corresponding carbon signals of the excess and minor diastereomer, respectively.

A similar de value was obtained when the reaction was carried out in ether or in benzene (entry 2,3). On the other hand, the chiral auxiliary was found to play an important role in determining the de value. The highest de value was obtained when 8-phenylmenthyl ester **6b** was employed, though the yield of the adducts **7b** was relatively low (entry 4). The bornyl ester **6c** showed poor diastereoselectivity (entry 5). The effect of the chiral auxiliary seems to be reasonably explained in terms of the concavity of the auxiliary [2].

The photoreaction of the menthyl ester **6a** with styrene (**8**) in acetonitrile at 30°C gave the



(3)



(4)

major stereoisomer of adduct **9** (eq 3), having a lower de value than that of the adduct **7a** obtained in the reaction with **2**. When α-methylstyrene (**11**) was used as the reaction partner of **6a**, two stereoisomers of [3+2]-adducts **12a**,**13a** were obtained in lower yields than that of **7a**, but with higher de values (eq 4). More pronounced diastereoselectivity, up to 61% de, was observed in the reaction of the 8-phenylmenthyl ester **6b** with **11** (eq 4). As for the effect of alkene structures on the diastereoselectivity of the [3+2]-photocycloaddition, the presence of the two substituents at one carbon atom of the double bond in the alkene structure and the steric bulk of the substituents seem to be of major importance.

Table 2

Temperature effect on the diastereoselectivity in the [3+2]-photocycloaddition of chiral 1,4-naphthalenedicarboxylic esters **6a,b** to isobutene (**2**).[a]

Entry	Ester	R*	Temperature (K)	Diasteremeric Ratio[b]	de (%)[c]
1	**6a**	Menthyl	273	1.89	31
2			288	1.70	26
3			303	1.59	23
4			318	1.44	18
5	**6b**	8-Phenylmenthyl	273	4.24	62
6			288	3.40	55
7			303	2.77	47
8			318	2.34	40

a Irradiation conditions are as follows; *hν* through an uranium filter (> 320 nm), irradiation time = 8h (entry 1-4) or 16h (entry 5-8), in MeCN, under N_2, [**6a,b**] = 2.0×10^{-3} mol/dm^3, [**2**] = 1.0 mol/dm^3.

b Diastereomeric ratio of **7a,b** determined by ^{13}C NMR analysis of the isolated mixture.

c Diastereomeric excess determined by de = (I - I') / (I + I'), where I and I' are the intensity of the corresponding carbon signals of the excess and minor diastereomer, respectively.

The temperature effect on the diastereoselectivity was examined in the [3+2]-photocycloaddition of **6a,b** to **2**, and the results are summarized in Table 2. The Table shows that the reaction temperature also plays an important role in determining the de value which increases considerably, up to 62% de, with decrease of the reaction temperature. Linear dependence of ln(diastereomeric ratio) on the reciprocal temperature (Eyring plots; ln(diastereomeric ratio) = $\ln(k/k') = -\Delta\Delta H^{\neq}/RT + \Delta\Delta S^{\neq}/R$, where k and k' were the overall rate constants for the formation of the excess and minor diastereomeric adducts **7a,b**, respectively) [1,2] was found in the reactions of **6a,b** (Figure 1). The calculated values of $\Delta\Delta H^{\neq}$ and $\Delta\Delta S^{\neq}$ are -0.061 kJ mol^{-1} and -0.15 J mol^{-1} K^{-1} for the reaction of **6a**, and -0.13 kJ mol^{-1} and -0.31 J mol^{-1} K^{-1} for the reaction of **6b**, respectively. These results indicate that there is no apparent change in the mechanism in the examined temperature range, and that under these conditions enthalpic factors, such as the steric effect in the reaction path, may make a predominant contribution to the diastereoselection.

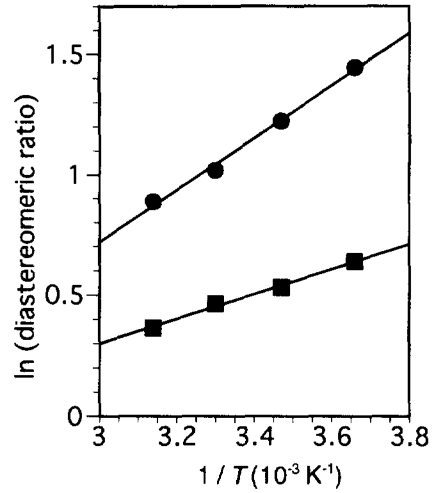


Figure 1. Eyring plot relating the diastereoselectivity to 1/T in the [3+2]-photocycloadditions of menthyl ester **6a** (■) and 8-phenylmenthyl ester **6b** (●) to isobutene (**2**).

In summary, the [3+2]-photocycloaddition of 1,4-naphthalenedicarboxylic esters, having easily removable chiral alcohol moieties, was found to have remarkable potential for diastereoselection. The diastereoselectivity was controlled by the concavity of the auxiliary, steric bulk of the substituents of alkenes, and reaction temperature.

References

[1] Inoue Y. Chem. Rev. 1992;92:741-770 and references cited therein.

[2] Buschmann H, Scharf H-D, Hoffmann N, Esser P. Angew. Chem. Int. Ed. Engl. 1991;30:477-515 and references cited therein.

[3] Haag D, Scharf H-D. J. Org. Chem. 1996;61:6127-6135. Faure S, Blanc SP-L, Piva O, Pete J-P. Tetrahedron Lett. 1997;38:1045-1048. Shepard MS, Carreira EM. J. Am. Chem. Soc. 1997;119:2597-2605. Crimmins MT, Choy AL. J. Am. Chem. Soc. 1997;119:10237-10238.

[4] Okada K, Samizo F, Oda M. Tetrahedron Lett. 1987;28:3819-3822.

[5] Sieburth SM, Joshi PV. J. Org. Chem. 1993;58:1661-1663. Sieburth SM, Hiel G, Lin C-H, Huan DP. J. Org. Chem. 1994;59:80-87.

[6] Hu S, Neckers DC. J. Org. Chem. 1997;62:564-567. Bach T, Jödicke K, Kather K, Fröhlich R. J. Am. Chem. Soc. 1997;119:2437-2445.

[7] Vaßen R, Runsink J, Scharf H-D. Chem. Ber. 1986;119:3492-3497.

[8] Scheffer JR, Yang J. CRC handbook of organic photochemistry and photobiology. Voca Raton: CRC Press, 1995:204-221.

[9] Mortezaei R, Awandi D, Henin F, Muzart J, Pete J-P. J. Am. Chem. Soc. 1988;110:4824-4826.

[10] Okada K, Sakai H, Oda M, Yoshimura A, Ohno T. J. Am. Chem. Soc. 1987;109:5534-5535. Okada K, Sakai H, Oda M, Yoshimura A, Ohno T. Tetrahedron Lett. 1989;30:1091-1094.

[11] Kubo Y, Inoue T, Sakai H. J. Am. Chem. Soc. 1992;114:7660-7663.