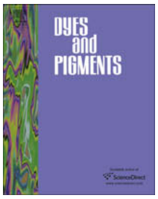
Dyes and Pigments 83 (2009) 262–265

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig



Short communication

Quantitative regio-selective Diels–Alder reaction of an unsymmetrical 1,4-dithiin and anthracene through heterogeneous solid state conversion

Ji Yeong Yun[a], Ja Jeong Koo[a], Do Kyung Lee[b], Jae Hong Kim[a,*]

[a] School of Display and Chemical Engineering, Yeungnam University, 214-1, Dae-dong, Gyeongsan, Gyeongsangbuk-do 712-749, Republic of Korea
[b] Gumi Electronics & Information Technology, Gumi, Gyeongsangbuk-do 730-853, Republic of Korea

ARTICLE INFO

Article history:
Received 29 September 2008
Received in revised form
25 November 2008
Accepted 28 November 2008
Available online 6 December 2008

Keywords:
Solid state reaction
Diels–Alder reaction
Regio-selective adduct
Charge-transfer complex
Heterogeneous conversion
Quantitative yield

ABSTRACT

The solid state, Diels–Alder reaction of an unsymmetrical 1,4-dithiin and anthracene produced an adduct regioselectively via a charge-transfer complex crystal prearranged to undergo a transformation among a constitutional isomeric mixture generated in the reaction solution. The heterogeneous solid state conversion allowed the reaction to proceed in almost quantitative yield.

Solid state reactions have attracted considerable attention on account of their enhanced stereo-selectivity and high product crystallinity under solvent free conditions [1–5]. In solid state reactions, the stereo-chemical structures and reactivity are controlled by the crystal lattices, fixed distance and orientation between the reaction centers, free spaces surrounding the reactant molecules, and reaction cavities [6,7]. Although a higher activation energy is required to initiate the chemical process in the solid state than in the solution state [8], it is believed that a practically useful solid state reaction can be expanded by exploiting intermolecular interactions, such as charge-transfer (CT), hydrophobic, π–π interaction and/or hydrogen bonding for the crystal lattice design [9].

In our previous paper, it was reported that a mono-phase single-crystal-to-single-crystal (SC-to-SC) Diels–Alder reaction between bis(*N*-methylimino)-1,4-dithiin and anthracene proceeded homogeneously in quantitative yield without any collapse of the crystal lattice during the entire conversion due to the flexibility of the 1,4-dithin ring [9]. This was attributed to anisotropic heterogeneous propagation in the heteromolecular CT crystal, which resulted in a quantitative product formation in the solid state reaction. This paper expands the mono-phase solid state conversion to obtain a regio-selective product using an unsymmetrical 1,4-dithiin molecule as an electron acceptor that improved solid state reaction yield and more importantly produced a regio-selective Diels–Alder adduct.

The unsymmetrical 1,4-dithiin (**2**) was synthesized by the cyclization and purified by a cyclization reaction of a 1:1 mixture (mole ratio) of methyl succinamic acid and propyl succinamic acid using a reported method [10]. The reaction produced three products containing bis(*N*-methylimino), bis(*N*-propylimino), and bis(*N*-methyl, *N*′-propylimino)-1,4-dithiin, (**2**), (**3**) and (**4**), respectively, which were separated by chromatography. Methyl and propyl groups were introduced into each imino moiety, in order to induce different steric effect during the crystallization and reaction process.

The Diels–Alder reaction between unsymmetrical 1,4-dithiin (**2**) and anthracene can generate constitutional isomers (**4**) and (**5**), as shown in Fig. 1.

The cycloaddition reaction of (**2**) with anthracene occurs readily in solution thermally via the 1:1 electron donor/acceptor (EDA) complex [11]. The EDA complex of unsymmetrical 1,4-dithiin (**2**) and anthracene was formed by mixing dichloromethane solutions of dithiin and anthracene in a 1:1 more ratio. UV–vis absorption spectra of the mixture solution showed that the CT band absorbed between 420 nm and 580 nm ($\lambda_{\max}$: 488 nm) where neither anthracene nor dithiin absorb, as shown in Fig. 2 [12–14].

---

[*] Corresponding author. Tel.: +82 53 810 2521; fax: +82 53 810 4631.
E-mail address: jhkim@ynu.ac.kr (J.H. Kim).

0143-7208/$ – see front matter © 2008 Published by Elsevier Ltd.
doi:10.1016/j.dyepig.2008.11.006

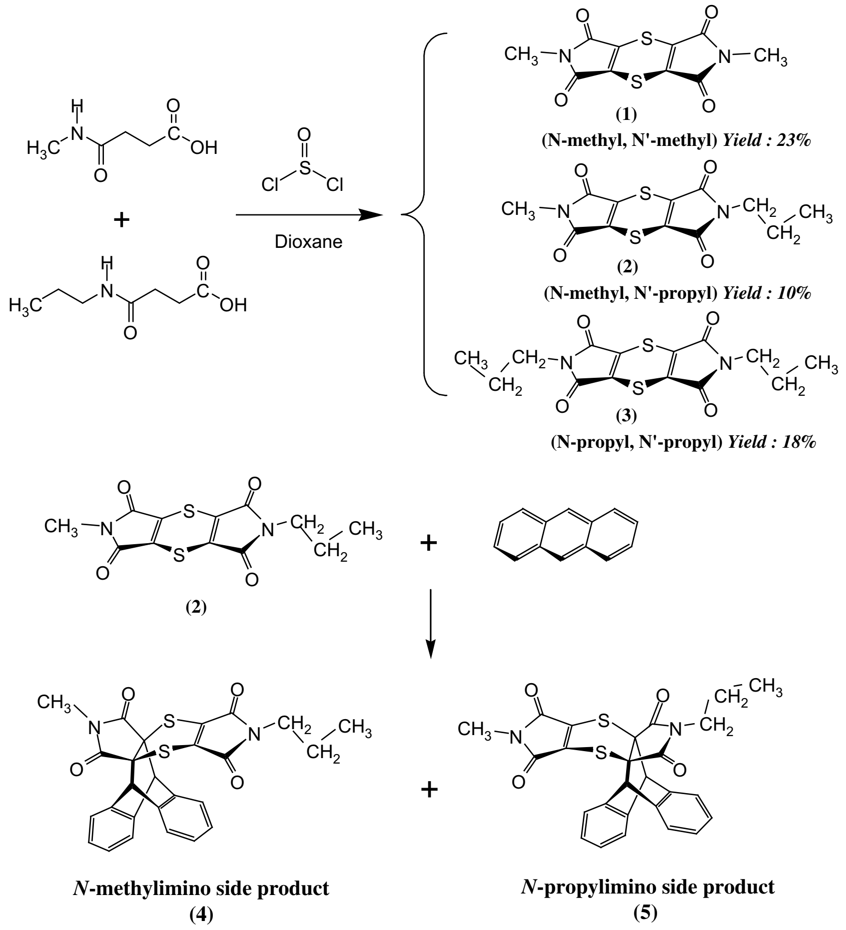


Fig. 1. Synthesis of the unsymmetrical-dithiin and their Diels–Alder reaction with anthracene.

Bis(*N*-methyl, *N*′-propylimino)-1,4-dithiin (**2**) and anthracene form an EDA complex in solution that further reacts thermally to yield a mixture of ragioisomers (**4** and **5**) of the Diels–Alder cycloadducts as shown in Fig. 1. In a solution state reaction, the formation ratio of two isomeric products, (**4**) and (**5**) was observed at a 3:1 mole ratio by ^{1}H NMR spectroscopy. The results indicate that the double bond of the *N*-methylimino group in dithiin reacts more easily with anthracene than with the *N*-propylimino group probably due to the enhanced steric hindrance of the propyl group (Fig. 3).

On the other hand, a single crystal of the EDA complex of 1,4-dithiin and anthracene was grown as a transparent dark brown

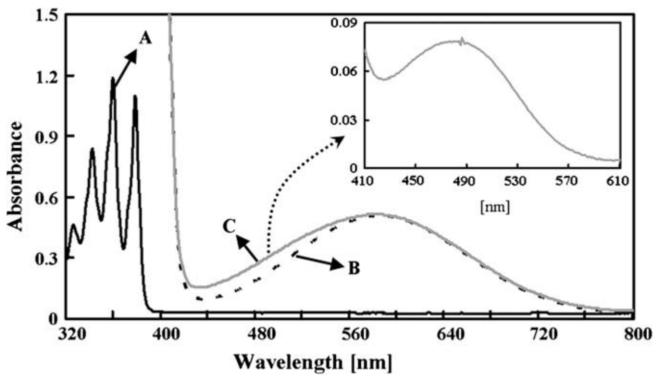


Fig. 2. Absorption spectrum of a dichloromethane solution of anthracene (A) unsymmetrical 1,4-dithiin (B), and their mixture (C). The in-set spectrum shows the EDA complex absorption band of 1,4-dithiin and anthracene.

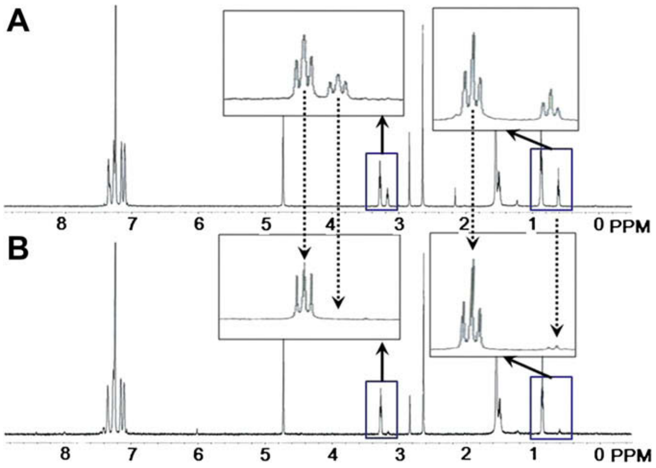


Fig. 3. ^{1}H NMR spectra of the solution state products mixture (A), and solid state reaction product (B) without any purification process.

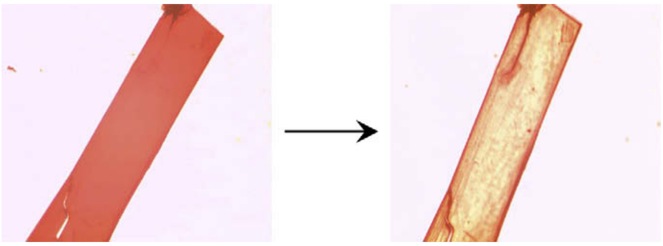


Fig. 4. Optical microscopy image of the solid state reaction phenomena.

Table 1
The Diels–Alder adduct formation ratio of 1,4-dithiin and anthracene in the solution and solid states.

	Solution state[a]		Solid state[a]	
Yield	30%		100%	
Selectivity	(**4**)[b]	(**5**)[b]	(**4**)[b]	(**5**)[b]
	75%	25%	100%	0%

[a] The Diels–Alder reaction condition.
[b] Chemical structure was shown in Fig. 1.

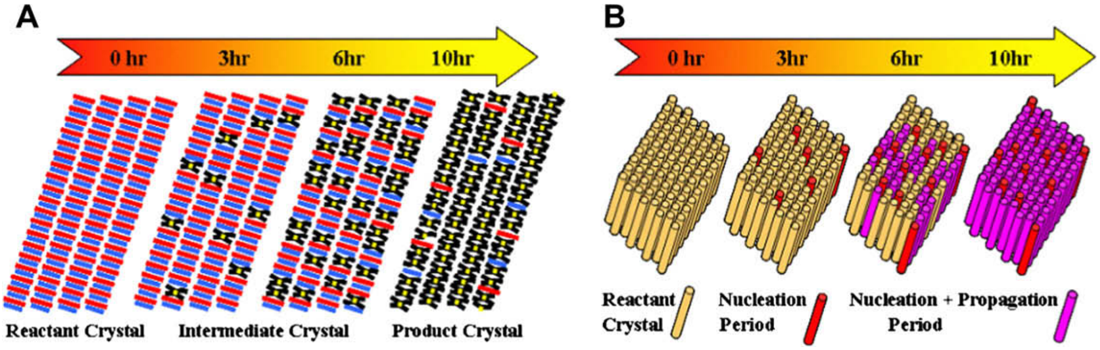


Fig. 5. The schematic representations of the homogeneous (A) and heterogeneous (B) solid state conversion.

plate by slow evaporation of the solvent from the mixed solution over a two week period in a 10 °C atmosphere. Unfortunately, the crystals were not suitable to perform X-ray single crystal analysis. However, it was possible to observe the solid state reaction phenomena using a microscope, as shown in Fig. 4. The solid state reaction did not diminish the quality of the crystals even after complete conversion.

The CT crystals reacted slowly even at room temperature to yield the [4+2] Diels–Alder cycloadduct. Heating the CT crystals at 70 °C resulted in the discharge of the initial brown color to a pale yellow over a 12 h period. This crude product from the solid state reaction was examined by ^{1}H NMR spectroscopy and compared with that of the solution state products. The results are summarized in Table 1.

The reaction proceeded almost quantitatively in the solid state and there was an isomeric form (**5**) in less than 1% in the resultant crystal which was compared with that in the solution state reaction to demonstrate that a heterogeneous crystalline transformation had occurred in entire crystal [15].

The schematic representations of the homogeneous (A) and heterogeneous (B) solid state conversion were shown in Fig. 5(A) and (B), respectively [9a,15b]. A theoretical analysis of the random bimolecular reactions in one-dimensional arrays such as homogeneous crystalline transformation showed that the solid state reaction yield cannot exceed 86.5% due to remaining starting molecules surrounded by product as shown in Fig. 5(A). In that case, the reactant surrounded by products with both sides could not react, and would be gradually accumulated during the reaction. As a result, the effective rate of the reaction slows down as compared to the simple first-order kinetics and the final chemical conversion never attains 100% [15a,16]. Therefore, only heterogeneous transformations, in which a product forms and grows topotactically within the original crystal phase, can produce a quantitative yield in a solid state reaction as shown in Fig. 5(B).

The center of anthracene should be positioned either below or on top of the *N*-methylimino moiety to yield a regio-selective product, (**4**) due to the steric effect of the *N*-propyl moiety. Furthermore, the solid state reaction occurred by heterogeneous propagation through the entire crystal, which produced a regio-selective Diels–Alder product. The thermodynamic approach, kinetic evaluations, and crystal analysis of reactant and product crystals are currently underway.

In conclusion, the regio-selective solid state reaction of unsymmetrical 1,4-dithiin and anthracene was achieved by a thermal Diel–Alder cycloaddition via a EDA complex crystal pre-arranged to undergo a transformation. It was possible to control the sterical effect in the reactant, which resulted in heterogeneous and quantitative product formation.

Acknowledgments

This study was supported by Grant No. R01-2007-000-20815-0 from the Basic Research Program of the Korea Science and Engineering Foundation.

References

[1] Addadi L, Mil JV, Lahav M. J Am Chem Soc 1982;104:3422.
[2] Cohen MD. Tetrahedron 1987;43:1211.
[3] Zimmerman HE, Zuraw MJ. J Am Chem Soc 1989;111:7974.
[4] Chung CM, Hasegawa M. J Am Chem Soc 1991;113:7311.
[5] McCullough Jr JD, Curtin DY, Paul IC. J Am Chem Soc 1972;94:874.
[6] (a) Addadi L, Lahav M. J Am Chem Soc 1979;101:2152;
(b) Leibovitch M, Olovsson G, Scheffer JR, Trotter J. J Am Chem Soc 1998;120:12755.
[7] Schmidt GM. Pure Appl Chem 1971;27:647.
[8] Therefore, most of the solid state transformations observed in literature heretofore are not thermal, bur rather are photoreactions such as photo-isomerizations and photo-cycloadditions.
[9] (a) Kim JH, Hubig SM, Linderman SV, Kochi JK. J Am Chem Soc 2001;123:87;
(b) Kim JH, Linderman SV, Kochi JK. J Am Chem Soc 2001;123:4951.
[10] Valla A, Cartier D, Zentz F, Labia R. Synthetic Comm 2006;36:3591. A mixture (1/1, mole ratio) of methyl succinamic acid and propyl succinamic acid was reacted with thionyl chloride in 1,4-dioxane using the reported method. The three products were separated by flash column chromatography (silicagel, $CHCl_3$/ethyl ether/hexane (1/3/6, v/v/v)); - bis(*N*-methylimino)-1,4-dithin (**1**): Yield; 23%, mp; 207 °C, ^{1}H NMR ($CDCl_3$); δ 3.01 (s, 6H), - bis(*N*-propylimino)-1,4-dithin (**3**): Yield; 18%, mp; 220 °C, ^{1}H NMR ($CDCl_3$); δ 3.46 (t, 4H, $J = 7.5$ Hz), 1.59 (sextet, 4H, $J = 7.5$ Hz), 0.89 (t, 6H, $J = 7.5$ Hz), - bis(*N*-methyl, *N*′-propylimino)-1,4-dithin (**2**): Yield; 10%, mp; 188 °C, ^{1}H NMR ($CDCl_3$); δ 3.44 (t, 2H, $J = 7.5$ Hz), 3.00 (s, 3H), 1.57 (sextet, 2H, $J = 7.2$ Hz), 0.87 (t, 3H, $J = 7.5$ Hz). Product (**4**): ^{1}H NMR ($CDCl_3$); δ 7.36–7.34 (m, 2H), 7.27–7.25 (m, 2H), 7.16–7.15 (m, 2H), 7.11–7.10 (m, 2H), 4.73 (s, 2H), 3.28 (t, 2H, $J = 8.4$ Hz), 2.64 (s, 3H), 1.50 (m, 2H), 0.86 (t, 3H, $J = 7.5$ Hz).

[11] (a) Draber W. Chem Ber 1967;100:1559;
(b) Hayakawa K, Mibu N, Osawa E, Kanematsu K. J Am Chem Soc 1982;104:7136.
[12] The EDA complex absorption generally occurs in the UV–vis region with $hc/\lambda_{CT} = IP - EA - \omega$, where IP is the ionization potential of the donor and EA is the electron affinity of the electron acceptor.
[13] Mulliken RS. J Am Chem Soc 1952;74:811.
[14] Mulliken RS, Person WB. Molecular complexes. New York: Wiley; 1969.
[15] (a) Wernick DL, Schochet S. J Phys Chem 1988;92:6773. and see Ref. [9];
(b) Kim JH, Jaung JY, Jeong SH. Opt Mater 2002;21:395.
[16] (a) Cohen ER, Reiss H. J Chem Phys 1963;38:680.