Journal of Molecular Structure 1098 (2015) 72–75

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Diels–Alder reactions: The effects of catalyst on the addition reaction

Özgür Yilmaz [a], Nermin Simsek Kus [a, *], Tuncay Tunç [b], Ertan Sahin [c]

[a] Department of Chemistry, Faculty of Arts and Sciences, Mersin University, 33343 Mersin, Turkey
[b] Department of Science Education, Faculty of Education, Aksaray University, 68100 Aksaray, Turkey
[c] Department of Chemistry, Faculty of Sciences, Atatürk University, 25240 Erzurum, Turkey

ARTICLE INFO

Article history:
Received 25 March 2015
Received in revised form
30 May 2015
Accepted 2 June 2015
Available online 6 June 2015

Keywords:
Diels–Alder addition
Cyclohexadiene
retro-Diels–Alder reaction
Substituted benzene

ABSTRACT

The reaction between 2,3-dimethyl-1,3-butadiene and dimethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate is efficiently achieved with small amounts of catalyst, i.e. phenol, AcOH, nafion, and β–cyclodextrin. *Exo*-diastereoselective cycloaddition reactions were observed both without catalyst and different catalysts for 48 days. As a result, different products (tricyclicmolecule **5**, *retro*-Diels–Alder product **6**, and oxidation product **7**) were obtained with different catalysts. In addition, we synthesized Diels–Alders product **8** and tricyclocyclitol **10** via Diels–Alder reaction. The structures of these products were characterized by ^{1}H NMR, ^{13}C NMR, MS and IR spectroscopy.

1. Introduction

The cycloaddition of alkenes and dienes known as the Diels–Alder reaction is a very useful method for forming substituted cyclohexenes [1–9]. The reactions are normally synchronous and processes are concerted. The cycloaddition products are traditionally affected by modest solvents and catalysts, in accordance with small changes in charge on going from reactants to the activated complex [7,10].

The aim of our study was to obtain the cycloaddition products of dienophile **3** with 2,3-dimethyl-1,3-butadiene (**4**) using different catalysts (phenol, acetic acid, nafion, and β–cyclodextrin) at room temperature, and also without catalyst at 25 and 40 °C, in addition to synthesizing the cyclitol and epoxide derivatives (**9**, **10**).

2. Experimental

2.1. Synthesis of dimethyl 7-oxo-bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (3)

Dimethyl 7-oxo-bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**6**) were prepared as described in the literature [11].

2.2. Diels–Alder reaction of dimethyl 7-oxo-bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (3) with 2,3-dimethyl-1,3-butadiene

Diene **3** (0.5 g, 2.4 mmol) and 2,3-dimethyl-1,3-butadiene **4** (0.197 g, 2.4 mmol) was dissolved in 10 mL of chloroform, and then the reaction was stirred at room temperature for 48 days. After the reaction, the solvent was removed to give product.

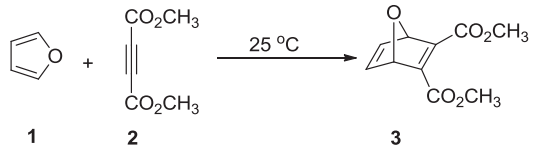
(1R,4S,4aS,8aR)-dimethyl 6,7-dimethyl-1,4,4a,5,8,8a-hexahydro-1,4-epoxynaphthalene-4a,8a-dicarboxylate (***5***): M. P.: 85–87 °C ($CHCl_3$), **δ_H (400 MHz, $CDCl_3$):** 6.52 (s, 2H), 4.65 (2H, s), 3.56 (6H, s), 2.48 A part of AB system (2H, d, $J = 14.0$ Hz), 2.41 B part of AB system (2H, d, $J = 14.0$ Hz), 1.73 (6H, s, $-CH_3$) **δ_C (100 MHz, $CDCl_3$,)** 173.9, 135.4, 126.9, 86.8, 63.2, 51.8, 40.2, 18.8, **Anal. Calc.** for $C_{16}H_{20}O_5$: C 65.74, H 6.9. Found: C 65.66H 6.32%, **MS *m/z***: 209 (M^+, $-CH_3$), 194, 193, 192, 191 (M^+,CH_3), 179, 178, 177 (M^+, $-CH_3$), 166, 165, 164, 163 (M^+, −O), 134, 133, 132 (M^+, −C), 122, 121, 120 (M^+,-O), 107, 106, 105, 104, 103 (M^+,-C), **IR (cm^{-1})** = 1716.7 (−C=O).

Dimethyl 4,5-dimethylcyclohexa-1,4-diene-1,2-dicarboxylate (***6***) [12]: **M. P:** 72–72.6 °C ($CHCl_3$), (Lit.63–66 °C), **δ_H (400 MHz, $CDCl_3$):** 3.78 (s, 6H), 2.92 (s, 4H), 1.66 (s, 6H), **δ_C (100 MHz, $CDCl_3$):** 168.4, 132.7, 121.5, 52.1, 34.1, 17.9.

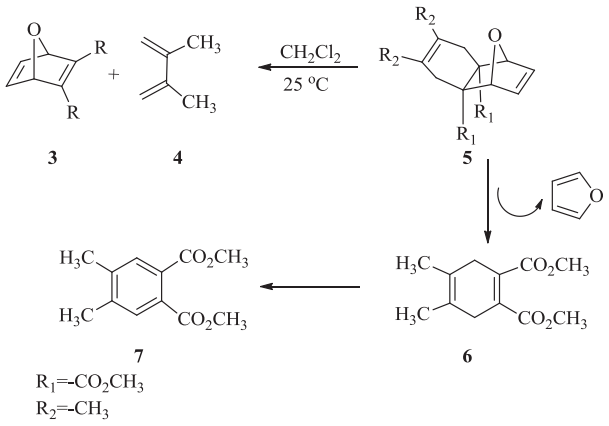
Dimethyl 4,5-dimethylphthalate (***7***) [12]: **M. P.:** 46–48 °C ($CHCl_3$) (Lit 56–57 °C) **δ_H (400 MHz, $CDCl_3$):** 7.42 (2H, s), 3.81 (6H, s), 2.24 (6H, s), **δ_C (100 MHz, $CDCl_3$):** 168.3, 140.2, 130.1, 129.4, 52.5, 19.7.

* Corresponding author.
E-mail addresses: simner@gmail.com, simner@mersin.edu.tr (N.S. Kus).

http://dx.doi.org/10.1016/j.molstruc.2015.06.012
0022-2860/



Scheme 1. Addition reaction of furan (**1**) and dimethyl acetylene dicarboxylate (**2**).



Scheme 2. Diels–Alder reaction of dienophile **3** and diene **4**.

2.3. Synthesis of (1aR,2R,2aS,7S,7aS)-dimethyl 4,5-dimethyl-1a,2,2a,3,6,6a,7,7a-octahydro-2,7-epoxynaphtho[2,3-b]oxirene-2a,6a-bis(carboperoxoate (*8*)

Diene **4** (0.500 g, 6.09 mmol) and epoxide **11** (1.38 g, 6.09 mmol) was dissolved in 10 mL of chloroform, and then the reaction was stirred at room temperature for 24 days. After the reaction, the solvent was removed to give 0.650 mg 95% yield of product **8**.

M. P.: 144–145 °C ($CHCl_3$), **δ_H (400 MHz, $CDCl_3$):** 4.23 (2H, s), 3.78 (2H, s), 3.61 (6H, s), 2.43 (2H, A part of AB system d, $J = 13.6$ Hz), 2.28 (2H, B part of AB system d, $J = 13.6$ Hz), 1.71 (6H, s), **δ_C (100 MHz, $CDCl_3$):** 172.7, 126.3, 82.8, 63.7, 52.1, 49.7, 39.3, 18.8, **Anal. Calc.** for $C_{16}H_{20}O_6$: C 62.33, H 6.54. Found: C 62.27, H 6.14%, **MS *m/z***: 308 (M^+, −2 O), 276 (M^+, $-CH_3$), 261, 262, 263 (M^+,-CO), 221, 220, 219, 218, 217 (M^+, $-CH_3$), 204, 203, 202, 201 (M^+, −CO), 177, 176, 174, 173 (M^+, $-2CH_3$) 147, 146, 145, 144, **IR (cm^{-1}):** 1716.3 (−C=O).

2.4. Synthesis of dimethyl 3,4-dimethyl-7-oxabicyclo[4.1.0]hept-3-ene-1,6-bis(carboperoxoate) (*9*)

Compound **5** (1.0 g, 3.42 mmol) was dissolved in 150 mL of chloroform, MCPBA (1.18 g, 6.84 mmol, 70%) was added, and then the reaction was stirred at reflux temperature for 3 days. The reaction mixture was added to 15 mL 50% $NaHSO_3$ solution and mixture was stirred for 15 min. The organic layer was separated and then washed with saturated aqueous $NaHCO_3$ (100 mL), dried with $MgSO_4$ and concentrated to give 740 mg of 90% yield of epoxide **9**.

M.P.: 64–65 °C ($CHCl_3$), **δ_H (400 MHz, $CDCl_3$):** 3.75 (6H, s), 2.86 (2H, d, $J_{2a,b} = J_{5a,b} = 19.6$ Hz), 2.64 (2H, d), 1,41 (s, 6H), **δ_C (100 MHz, $CDCl_3$):** 167.9, 131.3, 60.1, 52.3, 33.3, 19.1, **Anal. Calc.** for $C_{12}H_{16}O_5$: C 59.99, H 6.71, Found C 60.06, H 6.62%, **MS *m/z***: 240, (M^+, $-OCH_3$), 211, 210, 209, 208, 207, (M^+, −O), 194, 193, 192, 191, 190, (M^+, $-CH_3$), 179, 178, 177, 176, 175 (M^+,-CO), 151, 150, 149, 148, 147, (M^+, −CO), 123, 122, 121, 120, 119, (M^+, −O), 107, 106, 105, 104, 103, (M^+, −CO), **IR (cm^{-1}):** 1716 (−C=O).

2.5. Synthesis of (1R,2S,3R,4S,8aS)-dimethyl 2,3-dihydroxy-6,7-dimethyl-1,2,3,4,4a,5,8,8a-octahydro-1,4-epoxynaphthalene-4a,8a-dicarboxylate (*10*)

To a stirred solution of tricyclic molecule **5** (1,0 g, 3.42 mmol) in 10 mL of acetone/H_2O (1:1) were added NMO (0.409 g, 3.42 mmol) and 2 ml of OsO_4 ($7{,}87.10^{-3}$ mmol) at room temperature. The mixture was stirred vigorously at room temperature for 24 h. The reaction was stopped. Evaporation of solvent gave 1.06 g of *cis*-diol **10** with 95% yield.

M. P.: 170–171 °C ($CHCl_3$), **δ_H (400 MHz, $CDCl_3$):** 4.56 (2H, s) 4.12 (2H, s), 3.62 (6H, s, $-OCH_3$), 3.22 (2H, bs, 2–OH), 2.42 (2H, d,

Table 1
Diels–Alder reaction of dienophile **3** and diene **4** (Scheme 2).

		% yield									
Catalyst	**Product**	3 h	6 h	12 h	24 h	30 h	48 h	6. d	15. d	30. d	48. d
Non-catalyst 25 °C	**3**	65	45	30	10	0	0	0	0	0	0
	5	35	55	70	90	98	95	75	62	20	5
	6 [12]	0	0	0	0	2	5	25	33	68	80
	7 [12]	0	0	0	0	0	0	0	5	12	15
40 °C	**3**	35	25	10	0	0	0	0	0	0	0
	5	65	75	90	90	85	73	11	0	0	0
	6 [12]	0	0	0	10	15	27	84	89	47	8
	7 [12]	0	0	0	0	0	0	5	11	53	92
Acetic acid 25 °C	**3**	50	30	14	2	0	0	0	0	0	0
	5	50	70	86	98	90	80	55	20	0	0
	6 [12]	0	0	0	0	10	20	45	60	67	30
	7 [12]	0	0	0	0	0	0	0	20	33	70
***β*–cyclo dextrin 25 °C**	**3**	55	35	20	10	0	0	0	0	0	0
	5	45	65	80	90	95	90	60	30	0	0
	6 [12]	0	0	0	0	5	10	40	55	67	35
	7 [12]	0	0	0	0	0	0	0	15	33	65
Nafion-H 25 °C	**3**	60	40	27	8	0	0	0	0	0	0
	5	40	60	73	92	95	90	65	40	0	0
	6 [12]	0	0	0	0	5	10	35	50	70	43
	7 [12]	0	0	0	0	0	0	0	10	30	57
Phenol 25 °C	**3**	55	35	20	5	0	0	0	0	0	0
	5	45	65	80	95	95	85	60	30	0	0
	6 [12]	0	0	0	0	5	15	40	55	69	38
	7 [12]	0	0	0	0	0	0	0	15	31	62