Pergamon

Tetrahedron Letters, Vol. 35, No. 19, pp. 3111-3114, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $6.00+0.00

0040-4039(94)E0562-C

Ring Expansion Reaction of 2-Vinyl-4-methylene-1,3-dioxolanes to 4,5-Dihydro-3(2*H*)-oxepinones by Claisen Rearrangement

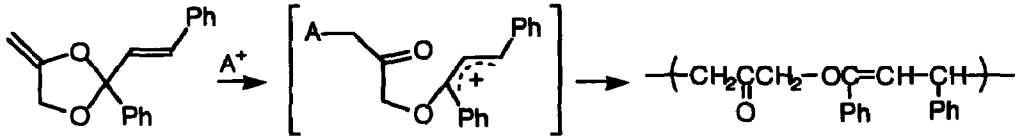
Jun-ichi Sugiyama*†, Kazuki Tanikawa†, Takashi Okada†, Kouichi Noguchi†, Mitsuru Ueda†, and Takeshi Endo‡

†Department of Materials Science and Engineering, Yamagata University,
4-3-16 Jounan, Yonezawa, Yamagata 992, *JAPAN*.

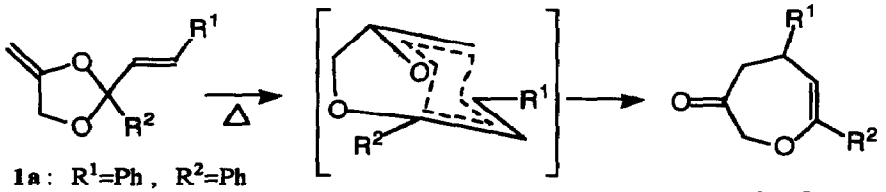
‡Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
4259 Nagatsuta-cho Midori-ku Yokohama 227, *JAPAN*.

Abstract: 2-Styryl or 2-vinyl substituted 4-methylene-1,3-dioxolanes underwent the Claisen rearrangement to obtain 4,5-dihydro-3(2*H*)-oxepinones in good yield. The rate of reaction followed the decreasing order: 2-phenyl-2-styryl > 2-phenyl-2-vinyl > 2-*tert*-butyl-2-styryl > 2-styryl.

Recently, we have reported[1] that the cationic polymerization of 4-methylene-2-phenyl-2-styryl-1,3-dioxolane (**1a**) can afford a 1,7-addition polymer (**2**) via double isomerization polymerization (eq. 1). In the course of our work on the free radical ring-opening polymerization of **1a**, we have found that **1a** is reluctant to undergo radical polymerization, but rearrange simply by heating to 4,5-dihydro-5,7-diphenyl-3(2*H*)-oxepinone (**4a**) (eq. 2). This synthetic method for 4,5-dihydro-3(2*H*)-oxepinone may be more advantage than using 2,3-sigmatropic shift of ylide provided from methylation-deprotonation of 6-benzoyl-3-oxothiane,[2] cyclization of 1-diazo-1-benzenesulfonylheptan-2,6-dione with rhodium acetate,[3] and deacetylation or desilylation of 4,5-dihydro-3-oxepinyl acetate or silyl ether.[4] Our reaction would provide a simple and effective approach to such ring system. This paper describes the ring expansion reaction of **1a** and its derivatives.[6]



1a **2** *eq 1*



1a: R^1=Ph, R^2=Ph
1b: R^1=H, R^2=Ph
1c: R^1=Ph, R^2=H
1d: R^1=Ph, R^2=^{t}Bu

3

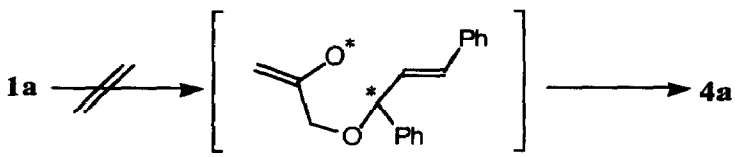
4a-d

eq 2

Reaction was carried out in a degassed sealed tube without solvents.[7] Structures of **4** were confirmed by IR, ^{1}H NMR and ^{13}C NMR. Results are summarized in table I. Although the reaction was so slow at 80 °C, **4a** could be obtained in low yield. **4a** could be afforded by raising the temperature to 120 °C in good yield. In the same condition, **1b** rearranged to **4b** for 6 h in 44% yield, while **1c** remained unchanged even after 48 h. Formation of **4c** was found to need heating above 180 °C. Reaction of alkyl substituted derivative **1d** was also slow and heating above 150 °C was necessary to afford **4d** in good yield. The rate of reaction followed the decreasing order: **1a** > **1b** > **1d** > **1c**.

Although this reaction seems to proceed by the concerted Claisen rearrangement since **1** has an allyl vinyl ether moiety and the reaction carried out by heating without a catalyst, the mechanisms through ionic or biradical intermediates (**5** or **6**) would be also possible in theory (eq. 3). Then, additional experiments were conducted in the presence of ethylene glycol, 2,5-di-*tert*-butyl-4-hydroxytoluene (BHT) or copper powder to trap an ionic or a biradical intermediate (run 4-6). However, the formation of **4a** could not suppressed by these additives. These results support that **1** undergo the concerted Claisen rearrangement to give **4**. A similar behavior of 5-membered ring system has been observed by Rhoads *et al.*[5] in the rearrangement of 2-methyl-2-vinyl-5-methylenetetrahydrofuran where 4-methyl-4-cycloheptenone was formed. They have proposed the mechanism through four-centered transition state which is a concerted active intermediate such as **3**.

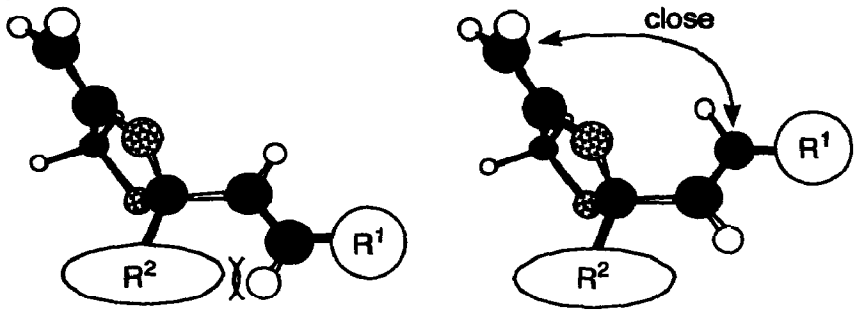
The findings described above indicate that substituent at 2-position of 1,3-dioxolane may play an important role in the rearrangement. It might be explained on the assumptions that 1) Compound **1** which substituted by bulky group on 2-position prefers conformation B to conformation A because of steric hindrance between R^2 and 2'-hydrogen of olefinic group (Scheme 1), or 2) interaction of 2C-3O σ*-bond with π-bond of phenyl group (**1a**, **1b**) or C-C σ-bond of *tert*-butyl group (**1d**) prompts rearrangement. The former assumption can explain the low reactivity of **1c** since contribution of conformation A retards the rearrangement, but can not explain the difference of reactivity between **1a** and **1d** which have a similar bulkiness. The transition state **3** where distortion ring strain is raised may be stabilized by the orbital interaction which enlarges the 2C-3O bond distance. The authors therefore proposed the latter assumption might be principal factor of rearrangement.



5 : * = - / +
6 : * = radical

eq 3

Scheme 1:



Conformation A ⇌ *Conformation B*

Table I. Claisen rearrangement of **1a-d**.

Run		Additive[a]	Temp.(°C)	Time(h)	Yield(%)[b]	
					4	recovery
1	**1a**	none	80	6	trace	100
2	**1a**	none	80	48	21	76
3	**1a**	none	120	6	84	8
4	**1a**	$HOCH_2CH_2OH$	120	3	90	trace
5	**1a**	BHT[c]	120	6	84	16
6	**1a**	Cu powder	120	6	78	7
7	**1b**	none	120	6	44	20
8	**1c**	none	120	48	0	100
9	**1c**	none	180	6	52	22
10	**1d**	none	120	24	10	90
11	**1d**	none	150	6	57	41

a)Equivalent mole or atom. b)Determined by ^1H NMR. c)2,5-Di-*tert*-butyl-4-hydroxytoluene.

Acknowledgment: We would like to thank Hitoshi Nagasawa and Sadao Kato (Yamagata University) for their technical assistance.

References and Notes

1. J. Sugiyama, S. Omokawa, M. Ueda, and T. Endo, *Makromol. Chem. Rapid Commun*, **1993**, *14*, 643-647.
2. E. Vedejs, T. H. Eberlein, and D. L. Varie, *J. Am. Chem. Soc.*, **1982**, *104* , 1445-1447.
3. V. Barre and D. Uguen, *Tetrahedron Lett.*, **1987**, *28*, 6045-6048.
4. (a)D. L. Clark, W.-N. Chou, and J. B. White, *J. Org. Chem.*, **1990**, *55*,.3975-3977. (b)W.-N. Chou, and J. B. White, *Tetrahedron Lett.*, **1991**,.*32*, 157-160.
5. (a)S. J. Rhoads, C. F. Brandenburg, *J. Am. Chem. Soc.*, **1971**, *93*, 5813-5815. (b)S. J. Rhoads, J. M. Watson, *ibid.*, **1971**, *93*, 5805-5813.
6. Materials: **1a** was prepared by previous method[1]. In the same way, **1b**, **1c**, and **1d** were also prepared from 1-phenyl-1-oxo-2-propene, cinnamaldehyde, or 4,4-dimethyl-1-phenyl-3-oxo-1-pentene by acetalization with epichlorohydrin in presence of boron trifluoride etherate followed by dehydrochlorination using potassium *tert*-butoxide, respectively. **1b**: yield 44%; IR (neat) 1690 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 3.90 (q, 1H, J=2.0 Hz, *E*-H-C=C-O), 4.41 (ddd, 1H, J=2.0, 2.0, 11.9 Hz

H-C-H (trans to 2-Ph)), 4.42 (ddd, 1H, J=2.0, 2.0, 1.7 Hz, *Z*-H-C=C-O), 4.52 (ddd, 1H, J=2.0, 1.7, 11.9 Hz H-C-H (cis to 2-Ph)), 5.31 (dd, 1H, J=1.0, 10.6 Hz, *Z*-H-C=C-), 5.40 (dd, 1H, J=1.0, 17.2 Hz, *E*-H-C=C-), 6.04 (dd, 1H, J=10.6, 17.2 Hz, H_2C=CH-), 6.9-7.6 (m, 5H, aromatic); ^{13}C NMR δ 66.5 (OCH_2), 78.6 (CH_2=C-O), 110.5 (O-C-O), 117.6 (CH_2=CH), 136.6 (CH_2=CH), 126.1, 128.2, 128.7 (aromatic CH), 139.0 (substituted aromatic carbon), 155.8 (=C-O). **1c**: yield 64%; IR (neat) 1688 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 3.91 (q, 1H, J=1.8 Hz, *E*-H-C=C-O), 4.3-4.6 (m, 3H, *Z*-H-C=C-O, CH_2-O), 5.69 (d, 1H, J=5.9 Hz, -O-CH-O-), 6.15 (dd, 1H, J=5.9, 16.0 Hz, CH=CHPh), 6.77 (d, 1H, J=16.0 Hz, CH=CHPh), 7.2-7.4 (m, 5H, aromatic); ^{13}C NMR δ 67.0 (CH_2-O), 78.2 (CH_2=C-O), 105.9 (O-C-O), 123.6 (CH=CHPh), 126.9, 128.5, (aromatic CH), 135.2 (CH=CHPh), 135.7 (substituted aromatic carbon), 155.6 (=C-O). **1d**: yield 35%; IR (neat) 1690 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.04 (s, 9H, *tert*-Bu), 3.82 (q, 1H, J=1.8 Hz, *E*-H-C=C-O), 4.35 (q, 1H, *Z*-H-C=C-O), 4.38 and 4.48 (dt, 1H+1H, J=11.8, 1.8 Hz, CH_2-O), 6.20 (d, 1H, J=15.8 Hz, CH=CHPh), 6.68 (d, 1H, J=15.8 Hz, CH=CHPh), 7.2-7.4 (m, 5H, aromatic); ^{13}C NMR δ 24.6 (C-CH_3), 38.3 (C-CH_3), 66.9 (CH_2-O), 77.2 (CH_2=C-O), 115.8 (O-C-O), 125.2 (CH=CHPh), 126.8, 128.0, 128.6 (aromatic CH), 132.0 (CH=CHPh), 136.8 (substituted aromatic carbon), 156.7 (=C-O).

7. Thermal reaction of **1** was carried out in degassed sealed Pyrex tube pretreated by washing with aq. $NaHCO_3$. Products and recovered materials were determined from ^1H NMR using benzaldehyde or cyclohexane as internal standards. **4a**: IR (neat) 1721 (C=O), 1644 (C=C) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.93 (ddd, 1H, J=0.9, 3.8, 12.1 Hz, H-CH-CHPh (trans to 5-Ph)), 3.50 (dd, 1H, J=10.8, 12.1 Hz, H-CH-CHPh (cis to 5-Ph)), 3.88 (ddd, 1H, J=3.8, 3.8, 10.8 Hz, CHPh), 4.52 (s, 2H, CH_2-O), 5.61 (dd, J=0.9, 3.8 Hz, CH=C), 6.9-7.6 (m, 10H, aromatic); ^{13}C NMR δ 41.4 (CHPh), 47.8 (CH_2-CHPh), 78.9 (CH_2-O), 110.3 (CH=CPh-O), 124.9, 127.0, 127.2, 128.2, 128.5, 128.7 (aromatic CH), 135.8, 143.5 (substituted aromatic carbon), 156.1 (=CPh-O), 209.5 (C=O). **4b**[2]: IR (neat) 1725 (C=O), 1655 (C=C) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.49 (dt, 2H, J=4.7, 6.5 Hz, CH_2-CH_2-C=O), 2.97 (t, 2H, J=6.5 Hz, CH_2-CH_2-C=O), 4.52 (s, 2H, O-CH_2-C=O), 5.55 (t, 1H, J=4.7 Hz, CH=C), 7.2-7.6 (m, 5H, aromatic); ^{13}C NMR δ 23.6 (CH_2-CH_2-C=O), 39.7 (CH_2-CH_2-C=O), 78.9 (O-CH_2), 106.2 (CH=CPh-O), 124.8, 128.3, 128.3 (aromatic CH), 136.1 (substituted aromatic carbon), 156.5 (=CPh-O), 211.2 (C=O). **4c**: IR (neat) 1721 (C=O), 1651 (C=C) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.89 (ddd, 1H, J=1.3, 3.6, 12.5 Hz, H-CH-CHPh (trans to 5-Ph)), 3.38 (dd, 1H, J=10.6, 12.5 Hz, H-CH-CHPh (cis to 5-Ph)), 3.71 (dddd, 1H, J=2.3, 3.6, 3.6, 10.6 Hz, CHPh), 4.34 and 4.38 (d, 1H+1H, J=17.8 Hz, CH_2-O), 4.91 (ddd, J=1.3, 3.6, 6.9 Hz, CH=CH-O), 6.59 (dd, J=2.3, 6.9 Hz, CH=CH-O), 7.2-7.3 (m, 5H, aromatic); ^{13}C NMR δ 40.2 (CHPh), 48.5 (CH_2-CHPh), 78.5 (CH_2-O), 114.2 (CH=CH-O), 126.9, 127.0, 128.6 (aromatic CH), 143.1 (substituted aromatic carbon), 147.5 (CH=CH-O), 209.5 (C=O). **4d**: IR (neat) 1725 (C=O), 1665 (C=C) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.13 (s, 9H, *tert*-Bu), 2.82 (ddd, 1H, J=1.0, 4.0, 11.9 Hz, H-CH-CHPh (trans to 5-Ph)), 3.39 (dd, 1H, J=10.9, 11.9 Hz, H-CH-CHPh (cis to 5-Ph)), 3.68 (ddd, 1H, J=3.6, 4.0, 10.9 Hz, CHPh), 4.29 and 4.36 (d, 1H+1H, J=17.8 Hz, CH_2-O), 4.87 (dd, J=1.0, 3.6 Hz, CH=C), 7.2-7.3 (m, 5H, aromatic); ^{13}C NMR δ 27.9 (C-CH_3), 37.0 (C-CH_3), 40.8 (CHPh), 48.0 (CH_2-CHPh), 79.1 (CH_2-O), 106.1 (CH=CBu-O), 126.8, 127.2, 128.7 (aromatic CH), 144.4 (substituted aromatic carbon), 166.4 (=CPh-O), 210.8 (C=O).

(*Received in Japan* 6 *August* 1993; *accepted* 12 *November* 1993)