This article was downloaded by: [BIBLIOTHEK der Hochschule Darmstadt] On: 24 November 2014, At: 08:04 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/lsyc20

Preparation and Reaction of Cyclic Oxalate of Diols

Kwan Soo Kim $^{\rm a}$, Eun Young Hurh $^{\rm a}$, Kyutae Na $^{\rm a}$ & Dai-II Chung $^{\rm a \ b}$

^a Department of Chemistry, Yonsei University, Seoul, 120-749, Korea

^b Department of Chemistry, Dong-a University, Pusan, Korea

Published online: 23 Sep 2006.

To cite this article: Kwan Soo Kim , Eun Young Hurh , Kyutae Na & Dai-II Chung (1991) Preparation and Reaction of Cyclic Oxalate of Diols, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 21:22, 2361-2367, DOI: <u>10.1080/00397919108021596</u>

To link to this article: http://dx.doi.org/10.1080/00397919108021596

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

PREPARATION AND REACTION OF CYCLIC OXALATE OF DIOLS

Kwan Soo Kim*, Eun Young Hurh, Kyutae Na, Dai-Il Chung[†]

Department of Chemistry, Yonsei University, Seoul 120-749, Korea

ABSTRACT : Cyclic oxalates were efficiently prepared by the reaction of diols with ethyl oxalyl chloride in the presence of triethylamine. They were stable under acidic conditions but cleaved to diols under basic conditions.

Although there are a great number of protective groups available for alcohols, cyclic protective groups such as cyclic acetals, cyclic ketals, cyclic orthoesters, and cyclic esters are more convenient for protection of polyhydroxy compounds in terms of efficiencies and selectivities compared to the usual acyclic protective groups for alcohols. Most of these

Copyright © 1991 by Marcel Dekker, Inc.

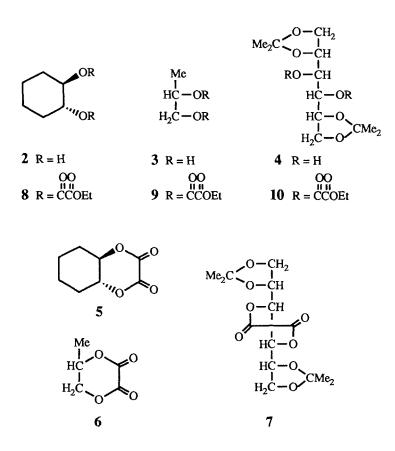
^{*} To whom correspondence should be addressed.

[†] Present address: Department of Chemistry, Dong-a University, Pusan, Korea

cyclic protective groups are unstable under acidic conditions and stable in basic medium whereas there are only a few acid-stable and baselabile cyclic protective groups are available such as 1,3-(1,1,3,3tetraisopropyldisiloxanylidene) derivatives¹ and cyclic carbonates.² We thought that the cyclic oxalate might be a useful acid-stable and base-labile protective group. Surprisingly, however, the cyclic oxalate has never been used for the protection of diols and the practical method for its preparation from diols is not available. Although there have been two reports for the preparation of cyclic oxalates from diols; one method by the reaction of diols with oxalic acid³ and another by the reaction of dioxastannolans with oxalyl chloride,⁴ these methods can not be applicable to other diols, especially to acid-labile complex polyfunctional compounds and the reactivity of the oxalate has not been examined.

The present communication describes an efficient method for the synthesis of cyclic oxalates from diols and usefulness of the cyclic oxalate as an acid-stable and base-labile protective group. We examined various possible oxalating agents for diols such as ethyl oxalyl chloride(1), oxalyl chloride, diethyl oxalate, oxalic acid, and 1,1'-oxalyl diimidazole. We have found that ethyl oxalyl chloride was the most satisfactory oxalating agent for diols. Diols used in this work were *trans* -1,2-cyclohexandiol(2), 1,2-propandiol(3), and 1,2;5,6-di-O-isopropylidene-D-mannitol(4) which represent a cyclic diol, an acyclic diol, and an acyclic diol containing an acid-labile protective group, respectively. A representative example is the reaction of diol 4 with 1. To a solution of compound 4 (0.50g, 1.9mmol)

and triethylamine (0.38g, 3.8mmol) in methylene chloride(10ml), ethyl oxalyl chloride (0.52g, 3.8mmol) was added dropwise with stirring at 0° C under nitrogen. After stirring at 0° C for 2 hrs, the reaction mixture was diluted with methylene chloride (30ml) and the organic phase was washed with water. The product in organic layer was purified by column



chromatography of silica gel to afford 1,2;5,6-di-*O*-isopropylidene-D-mannitol 3,4-oxalate (7)⁵(0.35g, 61%) and 1,2;5,6-di-*O*-isopropylidene-D-mannitol 3,4-bis(ethyloxalate)(10)⁶(0.15g, 17%).

Diol	Base	Product ^a	
		Cyclic Oxalate	Bis(ethyloxalate)
2	Et ₃ N	5 (65%)	8 (14%)
2	C_5H_5N		8 (88%)
3	Et ₃ N	6 (66%)	9 (7%)
3	C₅H₅N		9 (67%) [♭]
4	Et ₃ N	7 (61%)	10 (17%)
4	C_5H_5N		10 (70%) ^b

Table 1. Reactions of Diols with Ethyl Oxalyl Chloride

*Yields in parentheses are isolated ones.

^bA small amount of acyclic mono(ethyloxalate) was also detected.

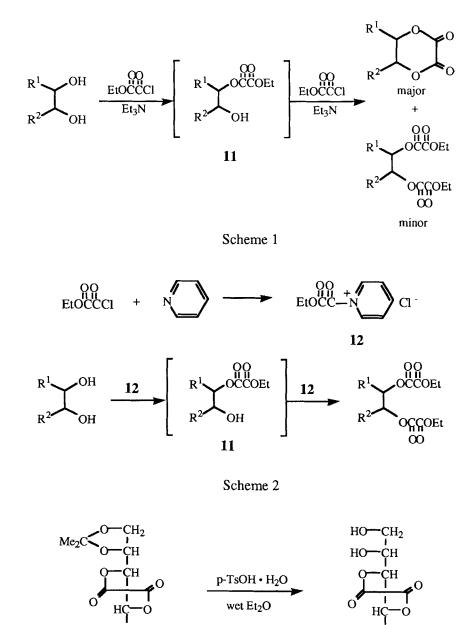
The product ratio of this reaction was very sensitive to the base employed. Thus, triethylamine provided cyclic oxalates as the major products whereas pyridine afforded only acyclic bis(ethyloxalate). The results are summarized in Table 1. Mono(ethyloxalate) 11 is a probable intermediate for the formation of both the cyclic oxalate and the acyclic bis(ethyloxalate) as shown in Scheme 1 and 2. In fact, it was observed that a small amount of acyclic mono(ethyloxalate) was produced in the reaction of diols 2 and 3 employing pyridine as a base. In the presene of triethylamine, the intramolecular cyclization of intertmediate 11 is faster than the further oxalation of a remaining hydroxy group of 11, whereas the formation of bis(ethyloxalate) is faster process in the presence of pyridine probably because ethyl oxalyl pyridinium salt 12 is very reactive species. It

HÇ

H₂Ċ

7

CMe₂







нс—он

H₂C-OH

13

is known that the acylpyridinium ion reacts more rapidly with the alcohol than the acid chloride.⁷

Deprotection of cyclic oxalates was readily accomplished. Cyclic oxalates 5, 6, and 7 were converted to the corresponding diols in almost quantitative yields at room temperature by various reagents ; (i) sodium methoxide in methanol, (ii) potassium carbonate in methanol, (iii) triethylamine in methylene chloride-water, or (iv) 1% aqueous sodium hydroxide in methylene chloride. On the other hand, cyclic oxalates were stable under acidic conditions. Thus, compounds 5 and 6 were not affected by p-TsOH \cdot H₂O in wet ether while two isopropylidene groups of compound 7 were cleaved to give rise to compound 13⁸ as shown in scheme 3.

REFERENCES AND NOTES

- 1. Markiewicz, W. T., J. Chem. Res. Synop., 1979, 24.
- Hough, L.; Priddle, J. E.; Theobald, R. S., Adv. Carbohydr. Chem., 1960, <u>15</u>, 91; Amarnath, V.; Broom, A. D., Chem. Rev., 1977, <u>77</u>, 183.
- Wilkinson, S. G., "Comprehensive Organic Chemistry," Stoddart, J. F., Ed., Pergamon Press, New York, 1979; Vol 1, p679.
- Davies, A. G.; Hua-De, P.; Hawari, J. A., J. Organomet. Chem., 1983, 256, 251.
- 5. Compound 7 ; TLC (SiO₂, ether) $R_f = 0.70$; mp 143-144°C; IR (KBr) 2980, 1790, 1760 cm⁻¹; ¹H NMR (CDCl₃) δ 1.36 (s, 6H), 1.97(s, 6H),

- 6. Compound **10** ; TLC (SiO₂, ether) R_f = 0.74; IR (KBr) 2980, 1760, 1740 cm⁻¹; ¹H NMR (CDCl₃); δ 1.2 (m, 18H, CH₃), 3.8-4.4 (m, 10H) 5.2-5.5 (dd, 2H).
- Fersht, A. R.; Jencks, W. P., J. Amer. Chem. Soc., 1970, <u>92</u>, 5432, 5442.
- Compound 13 ; TLC (SiO₂, 8:2 chloroform/methanol) R_f = 0.23; mp 180-181°C; IR (KBr) 3400, 1780 cm⁻¹; ¹H NMR (DMSO-d₆) δ3.4-3.7 (m, 6H), 3.7-4.2(m, 2H).
- 9. Financial support from the Korea Science and Engineering Foundation and the Organic Chemistry Research Center is gratefully acknowledged.

(Accepted in Japan 27 June, 1991)