ONE-POT PREPARATION OF γ-BUTYROLACTONE DERIVATIVES FROM OLEFINIC ALCOHOLS VIA INTRAMOLECULAR RADICAL CYCLIZATION REACTION

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Abstract —— γ-Butyrolactone derivatives were obtained in moderate yields to good yields via the radical decarboxylation of the mixed esters which were generated from olefinic alcohols by successive treatments with oxalyl chloride and N-hydroxy-2-thiopyridone.

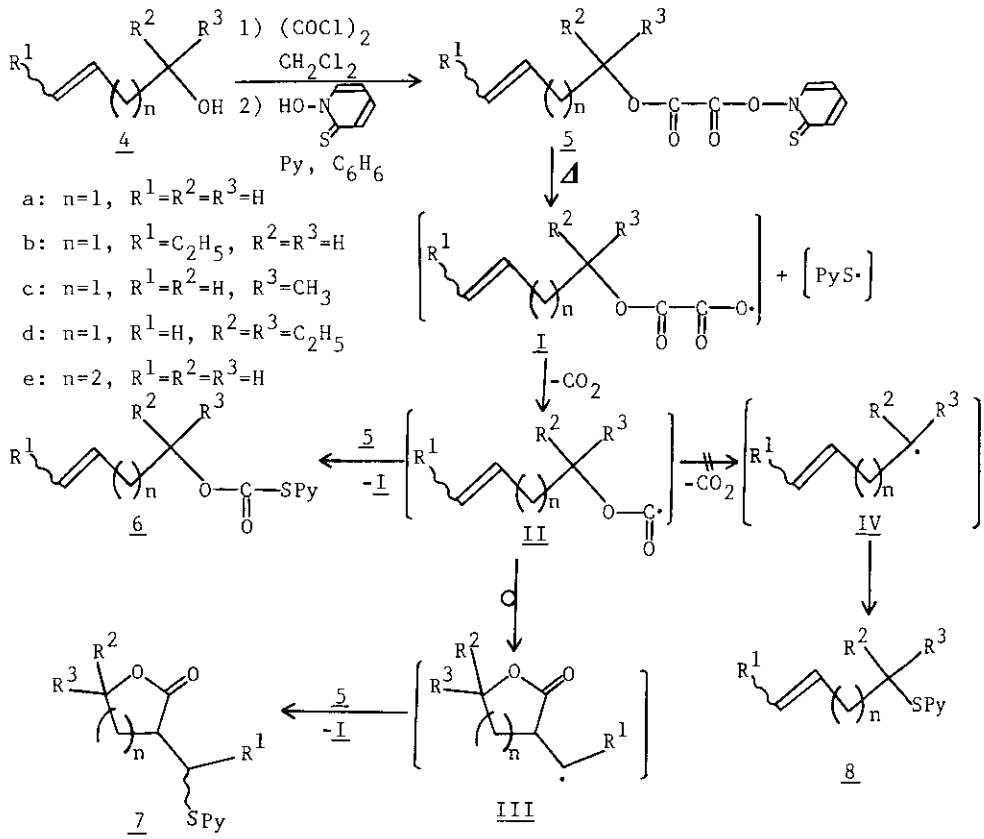
Recently, free radical reactions which mediate carbon-carbon bond formation in organic synthesis have been studied extensively.[1] In those reactions, Barton's reaction, which is the radical decarboxylative reactions of thiohydroxamic esters (O-acyl derivatives of N-hydroxy-2-thiopyridone) prepared from carboxylic acid chlorides and N-hydroxy-2-thiopyridone, is very attractive because the reaction procedure and purification of the reaction products are simple.[2] We studied this reaction for intermolecular carbon-carbon bond formation of these thiohydroxamic esters with active olefinic compounds.[3] While, a few reports on the same radical decarboxylative reaction with alcohols instead of carboxylic acids have been known.[4] But in those reports, the reactions only with tert-alcohols were studied to produce the corresponding tert-alkyl radicals.

As a part of our study directed toward the application of this decarboxylative reaction to other functional groups instead of carboxylic acids, we found the formation of γ-butyrolactone derivatives from olefinic alcohols in one-pot.

$$\underset{\underline{1}}{CH_3(CH_2)_7OH} \xrightarrow[2)\ \text{N-hydroxy-2-thiopyridone, Py, Solvent[S], reflux}]{1)\ (COCl)_2,\ CH_2Cl_2,\ \text{overnight}} \underset{\underline{2}}{CH_3(CH_2)_7\text{-O-C(=O)-SPy}} + \underset{\underline{3}}{CH_3(CH_2)_7\text{-S-Py}}$$

Solvent[S]	2(%)[5]	3(%)[5]
Benzene 40min	60	3
Toluene 30min	65	8
Chlorobenzene 10min	34	12

As a preliminary work, we carried out the reaction with octanol as above and obtained both compound 2 as a major product, which was formed by the reaction of carbonyl radical with the ester, and sulfide 3 as a minor product, which was the reaction product of double decarboxylated octyl radical with the ester. These results suggest that the formed alkoxycarbonyl radical may be captured by olefinic groups. Thus, when we carried out this reaction with 3-buten-1-ol 4a, the γ-butyrolactone derivative 7a, which was a very important component for a synthesis of natural products, was obtained in moderate yields via intramolecular cyclization as shown in both Table 1 and Scheme 1. A similar kind of reaction, which was the formation of α-methylene-γ-butyrolactone derivatives by the reaction of chlorocarbonates, Se-phenyl selenocarbonates, and S-methyl dithiocarbonates of homopropargylic alcohol derivatives with Bu_3SnH[6] and Bu_3SnH/Et_3B,[7] was recently reported. But in our system, γ-butyrolactone derivatives can be obtained in one-pot reaction from olefinic and acetylenic alcohols and this reaction does not need to use the toxic organotin compounds. γ-Butyrolactone derivatives 7c and 7d could be also obtained in moderate yields from sec- and tert-alcohols 4c and 4d, respectively. The typical procedure was carried out as follows. 5 ml of methylene chloride solution containing olefinic alcohol(2 mmol) were added to a stirred oxalyl chloride(0.8~1.5 ml) at room temperature and the mixture was stirred overnight. After the evaporation of solvent and excess oxalyl chloride, 4 ml of dry benzene were added to the residue and then 2.2 mmol of N-hydroxy-2-thiopyridone and 2 ml of benzene solution of pyridine(3 mmol) were added to the mixture and the resulting solution was stirred at 0°C for 30 min under nitrogen atmosphere. Then the reaction mixture was refluxed for 60 min. After the removal of solvent, compounds 6 and 7 were separated by column chromatography on silica gel. Next, the obtained lactone 7a was oxidized with m-CPBA(1.1 eq.) and the sulfoxide formed thus was heated at about 100°C under reducing pressure to give in 49% yield α-methylene-γ-butyrolactone, which was a natural product, tulipalin A, isolated from tulip bulbs.[8] Both trans and cis isomers of 3-hexen-1-ol 4b gave 7b in good yields and the ratio of formed diastereomers of 7b in both reactions were same. While, the use of 4-penten-1-ol 4e yielded thiolcarbonate 6e as a sole product. This result can be explained by the big difference in the cyclization rates between 3-butenoxycarbonyl radical IIa and 4-pentenoxycarbonyl radical IIe. Thus, the difference is deduced from the cyclization rates of 5-hexenyl radical($k=2.3 \times 10^5$ s^{-1} at 25°C) and 6-heptenyl radical($k=5.4 \times 10^3 s^{-1}$ at 25°C), respectively.[9]



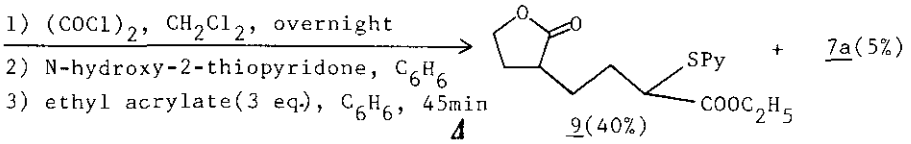
Scheme 1

Table 1. Reactions of Mediated Alkenoxycarbonyl Radicals.[a)]

Substrate	$(COCl)_2$	7[5)]	6[5)]
4a	0.8 ml	42%	1%
"	1.0 ml	51%	5%
"	1.5 ml	46%	4%
4b-trans	1.0 ml	71%(ratio=29:71)	7%
4b-cis	"	74%(ratio=29:71)	6%
4c	"	51%	4%
4d	" b)	43%	—
4e	"	0%	48%
"	" c)	18%	23%

a) The reactions were carried out in benzene for 60 min. b) The half ester from the reaction of oxalyl chloride with alcohol was prepared at room temperature for 60 min. c) Dropping procedure of half ester of oxalyl chloride into the sodium salt of N-hydroxy-2-thiopyridone over 4 h was used.

But the formation of δ-valerolactone could be accelerated by adding dropwise a half oxalyl ester(oxalyl monochloride of 4e) to the benzene solution of sodium salt of N-hydroxy-2-thiopyridone. By this procedure, δ-valerolactone was obtained in 18% yield. While β-propiolactone could not be obtained from allyl alcohol at all.



Further, the present reaction was carried out in the presence of ethyl acrylate to give in 40% yield ester 9,[5] which was formed via both intra- and intermolecular radical reactions, along with 7a. Finally α-pyridylthiomethylene-γ-butyrolactone was obtained in 40% yield from 3-butyn-1-ol by this system.

The formation of 7c and 7d means that the formed carbonyl radicals IIc and IId cyclize before the decarboxylation to alkenyl radicals IVc and IVd, and therefore the sulfides 8 were not formed. While the small amount (≤10%) of dialkenyl oxalates were observed after the reaction. Most of these products were formed by radical coupling reaction[10] of alkenoxycarbonyl radicals II because they were not formed during the preparation of 5.

Though the formed alkenoxycarbonyl radical II could be captured via intramolecular cyclization method with olefinic and acetylenic groups to give the corresponding γ-butyrolactone derivatives, it was disappointing not to get the intermolecular addition product of alkoxycarbonyl radical with ethyl acrylate or styrene by this method because of the formation of thiolcarbonate.

Further investigations on these and related reactions are now underway in this laboratory. We thank Prof. Derek H. R. Barton to give us encouragement to do this study.

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