CHEMISTRY LETTERS, pp. 283-284, 1981.

CONVERSION OF LACTONE INTO LACTONE HEMITHIOACETAL AND SYNTHESIS OF ENOL LACTONE

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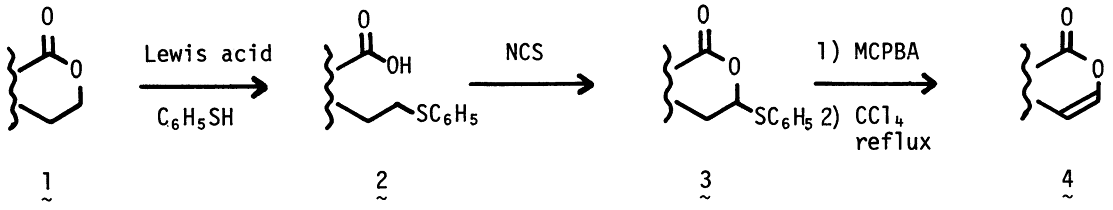
Lactone hemithioacetal was synthesized in good yield from ω-phenylthiocarboxylic acid derived from lactone, and it was converted into enol lactone *via* the corresponding sulfoxide.

The introduction of functional groups into the α-methylene group of lactone has been well established, because of the easy formation of its enolate anion. We now wish to report phenylsulfenylation at the ω-methylene group in lactone 1 followed by the conversion of the product 3 into enol lactone 4 as shown in Scheme.

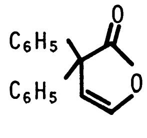


Scheme

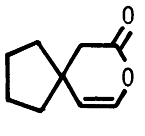
Five- or six-membered lactone was transformed into the corresponding ω-phenylthiocarboxylic acid 2 in acceptable yield by treatment with benzenethiol and Lewis acid ($AlBr_3$, BBr_3, or tri-n-butyltin triflate). The reaction required longer time and higher temperature compared to that with alkanethiol and Lewis acid,[1] because of lower nucleophilicity of benzenethiol than that of alkanethiol.

Successive conversion of the acid 2 into lactone hemithioacetal 3 was easily achieved by intramolecular cyclization reaction; the acid 2 on treatment with N-chlorosuccinimide in toluene or carbon tetrachloride under nitrogen afforded 3 in good yield.[2,3] The results were summarized in Table. The stereoisomers of 3c obtained from acid 2c were easily separated by preparative TLC in a 1:1 ratio.[4]

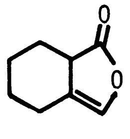
Oxidation of 3b and 3e with MCPBA followed by elimination by heating the resulting sulfoxide



4b



4e



4c

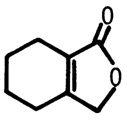


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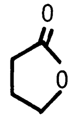
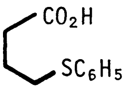
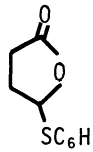
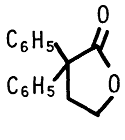
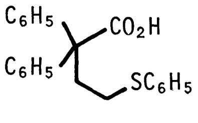
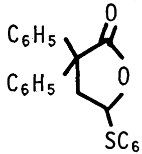
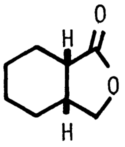
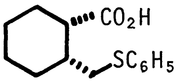
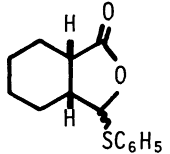
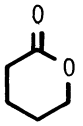
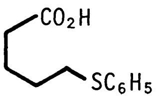
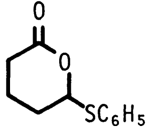
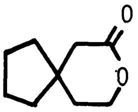
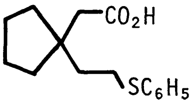
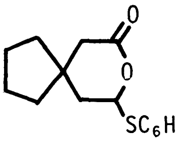
Table Conversion of lactone 1 to lactone hemithioacetal 3 *via* ω-phenylthiocarboxylic acid 2

ring opening of lactone 1[a]				Pummerer type reaction of 2[b]		
1	Lewis acid	(yield %)[c]	2	reaction time (h)	(yield %)[c]	3[c]
 1a	(n-Bu)$_3$SnOTf[d]	(54)	 2a	0.5	(83)	 3a
 1b	BBr$_3$	(69)	 2b	1	(85)	 3b
 1c	AlBr$_3$	(49)	 2c	1	(86)	 3c
 1d	AlBr$_3$	(31)	 2d	0.5[e]	(55)	 3d
 1e	AlBr$_3$	(49)	 2e	2[f]	(65)	 3e
1e	BBr$_3$	(49)	2e			

a) Reaction was carried out in benzenethiol unless otherwise noted. b) Acid 2 was treated with one molar equivalent of NCS in toluene at ambient temperature under nitrogen unless otherwise noted. c) Isolated yield. d) Co-solvent: dichloromethane. e) Reaction solvent: a 1:1 mixture of dichloromethane and carbon tetrachloride. f) Reaction solvent: carbon tetrachloride.

gave rise to enol lactones 4b and 4e in 70% and 63% yield, respectively. As expected, the sulfoxide derived from 3c (α-SC_6H_5) showed no change on prolonged heating in carbon tetrachloride. However another sulfoxide obtained from 3c (β-SC_6H_5) produced an unstable enol lactone 4c which was isomerized to $\alpha\beta$-unsaturated lactone 5[5] during isolation by preparative TLC (62% yield).

References and Notes

1) M. Node, K. Nishide, M. Sai, and E. Fujita, Tetrahedron Lett., 1978, 5211.
2) C. G. Kruse, E. K. Poels, F. L. Jonkers, and A. van der Gen, J. Org. Chem., 43, 3548 (1978).
3) The addition of triethylamine in order to scavenge hydrogen chloride produced during the reaction gave somewhat lower yield of 3.
4) 3c; α-SC_6H_5: NMR δ 5.63 ppm (1H, d, J = 3.9 Hz, $>C\underline{H}$-SC_6H_5); β-SC_6H_5: NMR δ 5.44 ppm (1H, d, J = 2.2 Hz, $>C\underline{H}$-SC_6H_5).
5) D. Butina and F. Sondheimer, Synthesis, 1980, 543.

(Received December 24, 1980)