CHEMISTRY LETTERS, pp. 923-926, 1979. Published by the Chemical Society of Japan

A NOVEL OXIDATIVE RING EXPANSION REACTION OF 2-ALKYLIDENE-1,3-DITHIANES INTO 3-ALKYL-1,4-DITHIEPAN-2-ONES WITH $Pb(OAc)_4$ 1)

Kunio HIROI and Shuko SATO
Tohoku College of Pharmacy, Sendai 983

The oxidative ring transformation reaction of 2-alkylidene-1,3-dithianes (1a-e) with $Pb(OAc)_4$ produced 3-alkyl-1,4-dithiepan-2-ones (2a-e) in fairly good yields. The reaction of 2-benzylidene-1,3-dithiane (1f) with $Pb(OAc)_4$ did not provide the corresponding ring expanded compound, instead giving 2-(α-acetoxybenzylidene)-1,3-dithiane (3) in 69% yield.

A ring expansion reaction of cyclic thioacetal derivatives should constitute an attractive route to other heterocycles containing sulfur in a main skeleton.

In a recent year there have been published several examples of the ring enlargement reaction of cyclic thioacetal derivatives by migration of the thio group with BF_3Et_2O,2) PPA,3) pyridine hydrochloride,4) P_2O_5,5) Cl_2,6) heating,7) and others.8)

In this communication we wish to represent a new alternative ring transformation of 2-alkylidene-1,3-dithianes into 1,4-dithiepane systems by an oxidative ring expansion reaction with $Pb(OAc)_4$.9)

An oxidative ring expansion reaction of 2-ethylidene-1,3-dithiane (1b) was investigated with 1.2 equivalents of $Pb(OAc)_4$ and the results were listed in Table I.

The reaction at 55° in benzene afforded the best yield (74%) of 3-methyl-1,4-dithiepan-2-one (2b).10), 11)

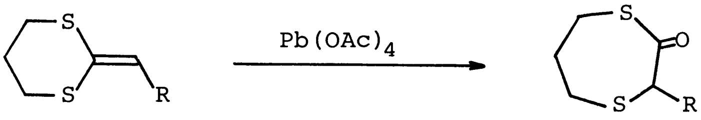
Other 2-alkylidene-1,3-dithianes (1a, 1c, 1d, and 1e), which were readily obtainable from 1,3-dithiane and carbonyl compounds,12) were treated with 1.2 equivalents of $Pb(OAc)_4$ in benzene at 55° for the reaction time described in Table II to produce 3-alkyl-1,4-dithiepan-2-ones (2a, 2c, 2d, and 2e)10), 13) respectively in the yields given in Table II.

The structures of the products were characterized by ir, nmr, and mass spectral

Table I. Oxidative Ring Expansion of 2-Ethylidene-1,3-dithiane (1b) with $Pb(OAc)_4$

Solvent	Reaction Temp.	Reaction Time, hr	Yield of 2b, %
C_6H_6	room temp.	12.0	55
C_6H_6	55°	16.5	74
C_6H_6	80°	12.0	47
$CHCl_3$	55°	8.0	65
CCl_4	55°	8.0	64

analyses. Furthermore, they were confirmed by the comparison of their spectra with those of the samples, which were prepared, though in very low yields, from α-chlorocarboxylic acid chlorides and 1,3-propanedithiol.



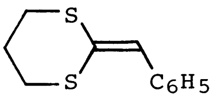
1a-e 2a-e

Table II. Oxidative Ring Expansion of 2-Alkylidene-1,3-dithianes (1) with $Pb(OAc)_4$

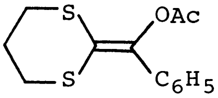
Starting Materials		Reaction Time,	Products (2)	
1	R	hr	Mp (°C)	Yield (%)
a	H	12.5	87-88	67
b	CH_3	16.5	54-55	74
c	CH_3CH_2	16.0	65-65.5	58
d	$CH_3CH_2CH_2$	14.5	60-61	59
e	$C_6H_5CH_2$	9.5	109-110	34

It should be noted, however, that the treatment of 2-benzylidene-1,3-dithiane (1f) with $Pb(OAc)_4$ did not give the expected ring expansion product, but gave 2-(α-acetoxybenzylidene)-1,3-dithiane (3)[14] in 69% yield. This compound was characterized by its conversion into 2-benzoyl-1,3-dithiane (4),[15] mp 92-92.5°, by hydrolysis, which was superimposable with the authentic sample, prepared from 1,3-dithiane and benzoyl chloride, in all respects of spectral data and mixed melting point determination.

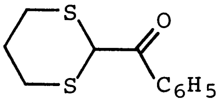
Recently, Lottenbach and Graf[16b] have reported on the reaction of 1f with $Pb(OAc)_4$ and proposed 2-acetoxy-3-phenyl-6,7-dihydro-5H-dithiepin (5) as the structure of the product. In view of the above result, however, we can conclude more definitely that



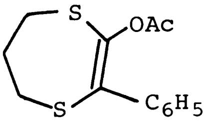
1f



3



4

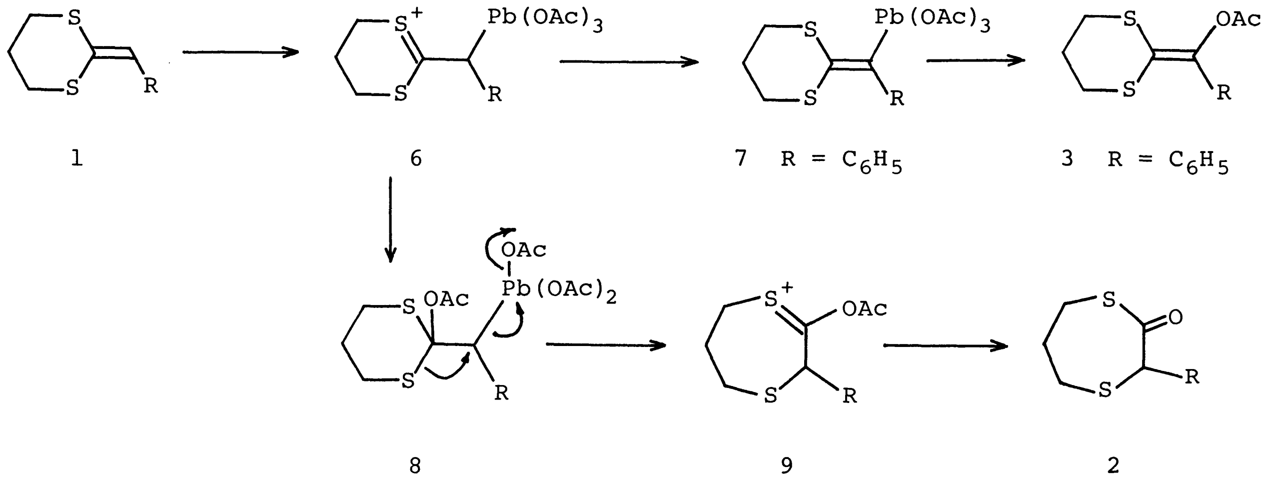


5

the structure proposed by them is wrong.

The reason of this result is not apparent, however this fact can be reasonably explained by preferable oxidation (6) of the benzylic part and stabilization by conversion into 7 with deprotonation.

The most possible pathway for this ring transformation reaction mentioned above is shown in the following scheme, involving a ring enlargement of the intermediate (8) by migration of the sulfur group and subsequent hydrolysis of 9.[16)]



1,4-Dithiepan-2-ones (2a-e) thus obtained could be transformed into α,β-unsaturated esters by oxidation ($NaIO_4$ in MeOH at room temp.) to sulfoxides followed by dehydrosulfenylation with thermolysis (refluxed in CCl_4 for 3 hr).[17)] This means that the 2-alkylidene-1,3-dithiane part in a molecule can be easily converted into α or α,β-functionalized carboxylic acid derivatives by the present procedures.

References and Notes

1) Preliminary results were presented at the 11th Congress of Heterocyclic Chemistry, Kanazawa, Japan, October 1978.

2) L.F. Fieser, C. Yuan, and T. Goto, J. Am. Chem. Soc., 82, 1996 (1960).

3) M. Tomoeda, M. Ishizaki, H. Kobayashi, S. Kanamoto, T. Koga, M. Inuzuka, and T. Furuta, Chem. Pharm. Bull. (Tokyo), 12, 383 (1964) and Tetrahedron, 21, 733 (1965).

4) G. Karmas, J. Org. Chem., 32, 3147 (1967).

5) J.L. Massingill, Jr., M.G. Reinecke, and J.E. Hodgkins, J. Org. Chem., 35, 823 (1970).

6) G.E. Wilson, Jr., and M-G. Huang, J. Org. Chem., 41, 966 (1976).

7) C.H. Chen, Tetrahedron Lett., 1976, 25 ; C.H. Chen and B.A. Donatelli, J. Org. Chem., 41, 3053 (1976) ; K. Hiratani, T. Nakai, and M. Okawara, Bull. Chem. Soc.,

Jpn., 49, 2339 (1976).

8) H. Rubinstein and M. Wuerthele, J. Org. Chem., 34, 2762 (1969) ; J.A. Marshall and H. Roebke, ibid., 34, 4188 (1969) ; H. Yoshino, Y. Kawazoi, and T. Taguchi, Synthesis, 1974, 713.

9) R.N. Butler, "Synthetic Reagents", Vol. 3, Ed. by J.S. Pizey, Ellis Horwood Limited, p. 277 (1977).

10) All new compounds gave satisfactory analytical data, which were in full agreement with the proposed structures. Melting points were uncorrected.

11) 2b : IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1662 (thio ester); NMR (CCl_4) δ: 1.35 (3H, d, J=7.0 Hz, CH_3), 1.80-2.65 (2H, m), 2.70-3.30 (4H, m, 2 SCH_2), 3.82 (1H, q, J=7.0 Hz, $\overset{O}{\overset{\|}{C}}$-CH-S); MS m/e : 162 ($M^+$).

12) P.F. Jones and M.F. Lappert, J. Chem. Soc., Chem. Commun., 1972, 526 ; D. Seebach, M. Kolb, and B-T. Gröbel, Chem. Ber., 106, 2277 (1973) ; D. Seebach and E.J. Corey, J. Org. Chem., 40, 231 (1975).

13) 2a : IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1660 (thio ester); NMR ($CDCl_3$) δ: 2.15-2.70 (2H, m), 2.75-3.25 (4H, m, 2 SCH_2), 3.60 (2H, s, $\overset{O}{\overset{\|}{C}}$-$CH_2$-S); MS m/e : 148 ($M^+$). 2c : IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1660 (thio ester); NMR (CCl_4) δ: 1.00 (3H, t, J=7.0 Hz, CH_3), 1.30-2.50 (4H, m), 2.50-3.30 (4H, m, 2 SCH_2), 3.60 (1H, t, J=7.0 Hz, $\overset{O}{\overset{\|}{C}}$-CH-S); MS m/e : 176 ($M^+$). 2d : IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1662 (thio ester); NMR (CCl_4) δ: 0.93 (3H, t, J=7.0 Hz, CH_3), 1.20-2.65 (6H, m), 2.70-3.35 (4H, m, 2 SCH_2), 3.68 (1H, t, J=7.0 Hz, $\overset{O}{\overset{\|}{C}}$-CH-S); MS m/e : 190 ($M^+$). 2e : IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1662 (thio ester); NMR ($CDCl_3$) δ: 2.00-2.60 (2H, m), 2.66-3.50 (6H, m, 2 SCH_2 and CH_2Ph), 3.95 (1H, t, J=7.0 Hz, $\overset{O}{\overset{\|}{C}}$-CH-S), 7.10-7.40 (5H, C_6H_5); MS m/e : 238 (M^+).

14) 3 : Bp 160°(1 mmHg) (oil bath); IR ν_{max}^{film} cm^{-1}: 1770 (enol ester), 1600 (phenyl); NMR (CCl_4) δ: 2.10 (3H, s, O-$\overset{O}{\overset{\|}{C}}$-$CH_3$), 1.80-2.26 (2H, m), 2.78 (t, J=6.0 Hz) and 2.90 (t, J=6.0 Hz, 4H, 2 SCH_2), 7.10-7.50 (5H, m, C_6H_5); MS m/e : 266 (M^+).

15) 4 : IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1680 ($\overset{O}{\overset{\|}{C}}$-$C_6H_5$), 1595, 1580 (phenyl); NMR ($CDCl_3$) δ: 1.90-2.30 (2H, m), 2.40-2.80 (2H, m) and 3.14-3.60 (2H, m, 2 SCH_2), 5.12 (1H, s, S-CH-S), 7.26-7.66 (3H, m) and 7.78-8.00 (2H, m, C_6H_5); MS m/e : 224 (M^+).

16) a) B.M. Trost and K. Hiroi, J. Am. Chem. Soc., 98, 4313 (1976) ; b) W. Lottenbach and W. Graf, Helv. Chem. Acta, 61, 3087 (1978).

17) B.M. Trost, T.N. Salzmann, and K. Hiroi, J. Am. Chem. Soc., 98, 4887 (1976).

(Received June 6, 1979)