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TETRAHYDROTHIOPYRAN-4-ONE. A USEFUL 5 C SYNTHON FOR THE SYNTHESIS OF 3-CYCLOPENTENONES

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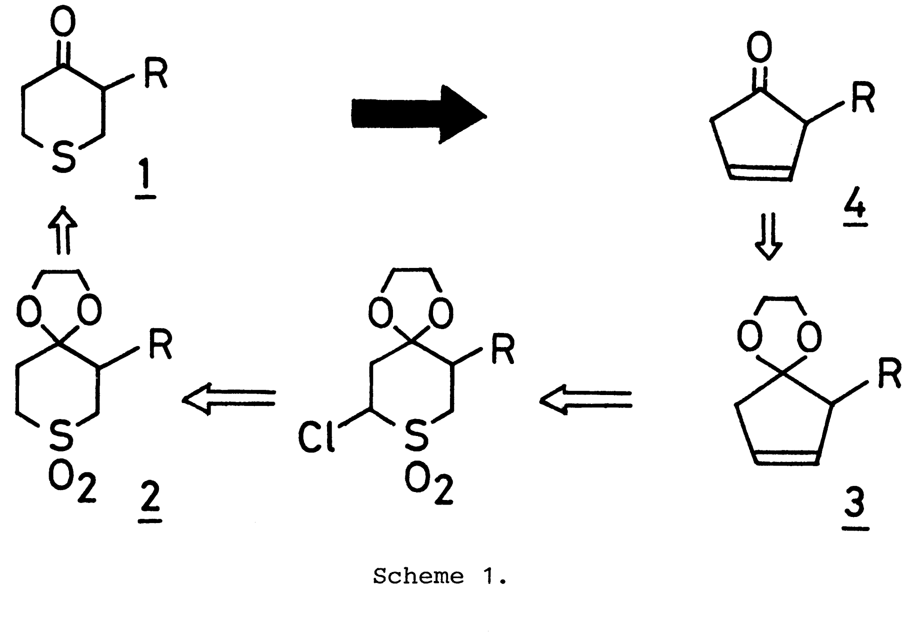
2-Alkyl-3-cyclopentenones were prepared in moderate yields starting from tetrahydrothiopyran-4-one by the one-pot Ramberg-Bäcklund reaction of 6-alkyl-1,4-dioxa-8-thiaspiro[4.5]decane 8,8-dioxides, followed by acid catalyzed de-dioxolanation.

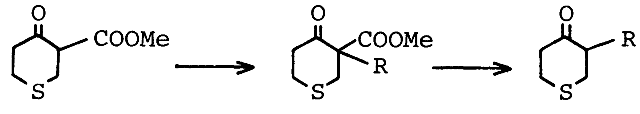
Many reactions of cyclic sulfur compounds have interesting synthetic potential.1) Tetrahydrothiopyran-4-one (1) (R=H)2) is constituted of 5 carbon unit and a sulfur atom as an active functional group for ring transformation. Recently, Jones et al. utilized 1 for the synthesis of optically active alcohols by enzymic reduction of carbonyl group, followed by desulfurization with Raney nickel.3)

In connection with our jasmonoids (important fragrant compounds such as methyl jasmonate and methyl dihydrojasmonate) synthesis, we examined the possible route (Ramberg-Bäcklund reaction) to 3-cyclopentenones (4) from 6-alkyl-1,4-dioxa-8-thiaspiro[4.5]decane 8,8-dioxides (2) as shown in Scheme 1.4) We now wish to report a simple synthetic method for 3-cyclopentenones (4) starting from an easily available tetrahydrothiopyran-4-one (1) as a 5 C synthon.



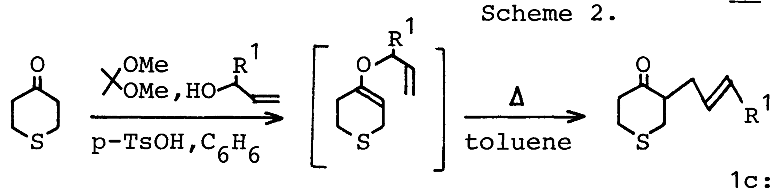
Scheme 1.

Starting materials, 3-alkyltetrahydrothiopyran-4-ones (1),[6] were prepared by two procedures; (a) alkylation of 3-methoxycarbonyltetrahydrothiopyran-4-one with alkyl halides (RX, K_2CO_3, acetone-reflux[7] or potassium enolate isolated, RX, DMSO, 25 °C[8]), followed by demethoxycarbonylation (LiCl, HMPA, 80 °C[9]) (Scheme 2), and (b) allylation by Claisen rearrangement of allyl vinyl ether[10] (Scheme 3).



Scheme 2.

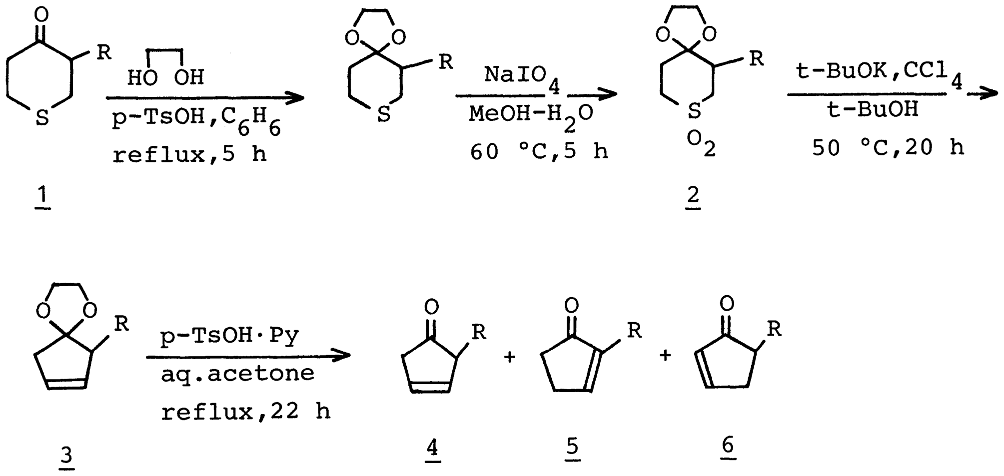
1a: R= CH_2Ph(65%)
1b: R= C_5H_{11}-n(60%)



1c: R^1= H(92%)
1d: R^1= C_2H_5(68%)

Scheme 3.

In Scheme 4, tetrahydrothiopyran-4-ones (1) were quantitatively converted into 6-alkyl-1,4-dioxa-8-thiaspiro[4.5]decane 8,8-dioxides (2)[11] by protection of carbonyl group (ethylene glycol, p-TsOH(cat.), C_6H_6-reflux), followed by oxidation ($NaIO_4$(3 equiv.), methanol-water, 60 °C). 6-Membered sulfones (2) were transformed into cyclopentenes (3)[12] by the one-pot Ramberg-Bäcklund reaction[13] (t-BuOK, CCl_4, t-BuOH, 50 °C) under nitrogen in moderate yields (Table 1). After cleavage of 1,3-dioxolane of 3 by acid catalyzed de-dioxolanation (p-TsOH•Py(cat.), aq. acetone-reflux),[14] 3-cyclopentenones (4) were obtained as major components (>90%) with minor amounts of 2- and 4-cyclopentenone isomers. A pure 3-cyclopentenone (4)[15] was isolated by Florisil column chromatography (Table 2).



Scheme 4.

This synthetic approach from 1 to 4 offers several advantages.
(i) The starting materials 1 and reagents used are readily available; (ii) all operations in the reaction steps (1→2→3→4) are simple; (iii) the yields are moderate to good.

Table 1. Cyclopentene 3 obtained by the one-pot Ramberg-Bäcklund reaction

Sulfone (2)	Yield of 3 /%
a, R= CH_2Ph	69
b, C_5H_{11}-n	40
c, CH_2-CH=CH_2	73
d, CH_2-CH=CH-C_2H_5	77
e, C_3H_7-n [a)]	60

a) 2e was prepared by hydrogenation (H_2/Pt) of 2c.

Table 2. 3-Cyclopentenone 4 obtained by acid catalyzed de-dioxolanation of 3

Cyclopentene (3)	Isomer ratio[a)] (4) : (5 + 6)	Isolated yield of 4 /%
a, R= CH_2Ph	91 : 9	53
b, C_5H_{11}-n	94 : 6	78
c, CH_2-CH=CH_2	97 : 3	84
d, CH_2-CH=CH-C_2H_5	88 : 12	79
e, C_3H_7-n	91 : 9	70

a) Determined by GC before purification of 4.

In a typical experiment, potassium tert-butoxide (20 mmol) was added by portions to a stirred solution (CCl_4(10 ml)-t-BuOH(5 ml)) of sulfone 2d (2 mmol) at 50 °C under nitrogen and the mixture was stirred for 20 h at 50 °C. The usual workup and purification by silica gel column chromatography (hexane : ether = 3 : 1) gave 3d in 77% yield. A solution of an oily 3d (1 mmol) and catalytic pyridinium p-toluenesulfonate (p-TsOH·Py, 20 mg) in aqueous acetone (30 ml; water : acetone = 1 : 4) was refluxed for 22h, and the usual workup, followed by purification with Florisil column chromatography (hexane : ether = 4 : 1) gave 3-cyclopentenone 4d in 79% yield.

In conclusion, the presented results suggest that tetrahydrothiopyran-4-one (1) is a useful 5 C synthon for the synthesis of 3-cyclopentenones (4). 3-Cyclopentenone (4) can be easily converted into 2-cyclopentenone by known procedure.[5b)] Applications of this procedure to the jasmonoids synthesis are now in progress.

References

1) E. Vedejs and G. A. Krafft, Tetrahedron, 38, 2857 (1982).

2) H. M. E. Cardwell, J. Chem. Soc., 1949, 715.

3) J. Davies and J. B. Jones, J. Am. Chem. Soc., 101, 5405 (1979).

4) We also reported the synthesis of 2-alkyl-2-cyclopentenones starting from tetrahydrothiopyran-4-one (1) by means of acid catalyzed cyclization (H_3PO_4, HCOOH) of divinyl ketones; H. Matsuyama, Y. Miyazawa, Y. Takei, and M. Kobayashi, the abstracts of the 12th Symposium on Organic Sulfur and Phosphorus Chemistry, Osaka, January (1984), p. 83.

5) Typical procedures for the synthesis of 3-cyclopentenones;
   a) Pd(0) catalyzed reaction of 1,3-diene epoxide; M. Suzuki, Y. Oda, and R. Noyori, J. Am. Chem. Soc., 101, 1623 (1979);
   b) Jones oxidation of cyclopentenol; P. A. Grieco, J. Org. Chem., 37, 2363 (1972);
   c) Thermolysis of vinyl cyclopropane; E. J. Corey and S. W. Walinsky, J. Am. Chem. Soc., 94, 8932 (1972).

6) 1a: IR(neat) 1705 cm^{-1} (C=O). 1b: IR(neat) 1705 cm^{-1} (C=O). 1c: bp 79-80 °C /1.5 mmHg; IR(neat) 1705 cm^{-1} (C=O). 1d: bp 114 °C/5 mmHg (E-2-pentenyl derivative); IR(neat) 1715 (C=O), 970 cm^{-1}; ^{1}H-NMR(CDCl$_3$) δ0.92 (3H, t, J=7.2 Hz), 1.67-3.00 (11H, m), 5.10-5.46 ppm (2H, m).

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8) T. Takemura and J. B. Jones, J. Org. Chem., 48, 791 (1983).

9) P. Müller and B. Siegfried, Tetrahedron Lett., 1973, 3565.

10) Organic Syntheses, Coll. Vol. 5, pp. 25 and 292; preparation of 2-allylcyclohexanone.

11) 2a: mp 175.5-176.5 °C; IR(KBr) 1290, 1140 cm^{-1} (SO$_2$). 2b: mp 92.5-93.6 °C; IR(KBr) 1290, 1135 cm^{-1} (SO$_2$). 2c: mp 100.3-102.3 °C; IR(KBr) 1290, 1120 cm^{-1}. 2d: mp 109.5-100.0 °C; IR(KBr) 1290, 1135 (SO$_2$), 970 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ0.93 (3H, t, J=7.2 Hz), 1.54-3.25 (11H, m), 3.85 (4H, s), 5.00-5.41 ppm (2H, m). 2e: mp 105.5-106.5 °C; IR(KBr) 1290, 1110 cm^{-1}.

12) ^{1}H-NMR (CDCl$_3$) of cyclopentene 3 (6-alkyl-1,4-dioxaspiro[4.4]non-7-ene) shows a new peak at δ5.60 ppm (CH=CH, multiplet).

13) L. A. Paquett, Org. React., 25, Chap. 1 (1977).

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15) 4a: IR(neat) 1745 (C=O), 1600 cm^{-1}; ^{1}H-NMR(CDCl$_3$) δ2.70-2.81 (3H, m), 3.65-3.85 (2H, m), 5.94 (2H, s), 7.19 ppm (5H, s). 4b: IR(neat) 1745 cm^{-1} (C=O); ^{1}H-NMR(CDCl$_3$) δ0.61-1.90 (11H, m), 2.57-3.08 (3H, m), 6.07 ppm (2H, s). 4c: IR(neat) 1740 cm^{-1} (C=O); ^{1}H-NMR(CDCl$_3$) δ1.95-3.10 (5H, m containing br-s at 2.74), 4.78-5.26 (2H, m), 5.51-6.23 (3H, m containing br-s at 6.06). 4d: IR(neat) 1740 (C=O), 970 cm^{-1}; ^{1}H-NMR(CDCl$_3$) δ0.91 (3H, t, J=7.2 Hz), 1.70-2.97 (7H, m containing s at 2.80), 5.34-5.55 (2H, m), 6.05 ppm (2H, s). 4e: IR(neat) 1745 cm^{-1} (C=O); ^{1}H-NMR(CDCl$_3$) δ0.65-1.70 (7H, m), 2.35-2.88 (3H, m), 6.07 ppm (2H, s).

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