Tetrahedron Letters, Vol.30, No.2, pp 189-192, 1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Pergamon Press plc

INTRAMOLECULAR ENE REACTION OF UNSATURATED THIOKETONES

Shinichi Motoki,* Tsumoru Watanabe, and Takao Saito

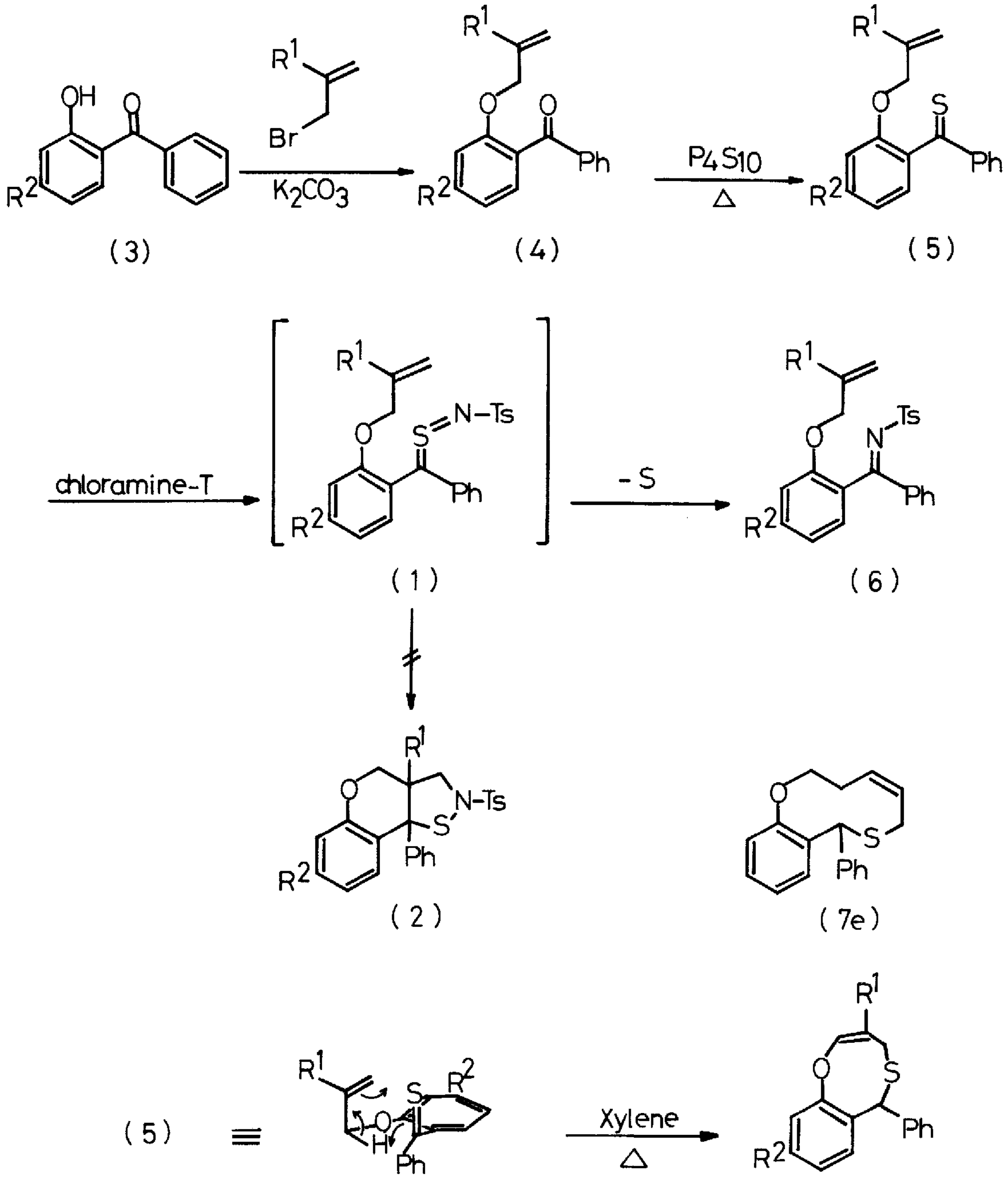
Department of Chemistry, Faculty of Science, Science University
of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162 JAPAN

Abstract: The thermal cyclization of o-(2-substituted allyloxy)thiobenzophenones giving 1,5-oxathiocine derivatives is reported. This is the first example of the new type intramolecular ene reaction of unsaturated thioketones.

Thione S-imides possess the property of 1,3-dipolar compounds and react with a variety of compounds to give the corresponding sulfur containing five membered ring compounds.[1,2,3] On the other hand, conversion of β -amionovinylaryl thione S-imides[4] and N-benzoyl-S-(9-fluorenylidene)sulfilimine[1] to the thiazoline and oxathiazoline derivatives has been reported as examples of the intramolecular 1,3-dipolar cycloaddition reaction of thione S-imides.

Interest in these results has led to the suggestion that the cyclization of o-(2-substituted allyloxy)diarylthione S-imides (1) would give the bicyclic compounds 2. Synthesis of 1 from o-hydroxy benzophenone derivatives (3) was planned according to the sequence (3)-(4)-(5)-(1). However, treatment of the thione 5 with chloramine salt afforded the imine 6 presumably as a result of loss of sulfur from 1. On the other hand, it was found that treatment of the ketone 4a with P_4S_{10} in refluxing THF afforded the 1,5-oxathiocine derivative 7a (2%) together with the desired thioketone 5a (43%). The mass spectrum of 7a showed the molecular ion peak at m/e 254. The ^{1}H-NMR spectrum showed the signals of a methine proton at δ 5.79(1H, s), two olefinic protons at 4.69(1H, ddd, J=9.3, 9.3, 7.7 Hz) and 6.48(1H, dd, J=7.7, 1.4 Hz) and two unequivalent methylene protons at 2.76(1H, dd, J=14.6, 9.3 Hz) and 2.96(1H, ddd, J=14.6, 9.3, 1.4 Hz) with the corresponding ^{13}C-NMR signals at δ 45.11 (d), 101.21(d), 145.09(d) and 24.92(t).

As we were interested in this reaction, the thermal cyclization of thiones 5a-d was examined. Upon heating 5a-d in refluxing xylene, products 7a-d were obtained in high yields.[5] Similarly, o-(4-pentenyloxy) thiobenzophenone obtained from 3a and 5-bromo-1-pentene also afforded the ten-membered ring product 7e[5]. Results are summarized in Table 1.

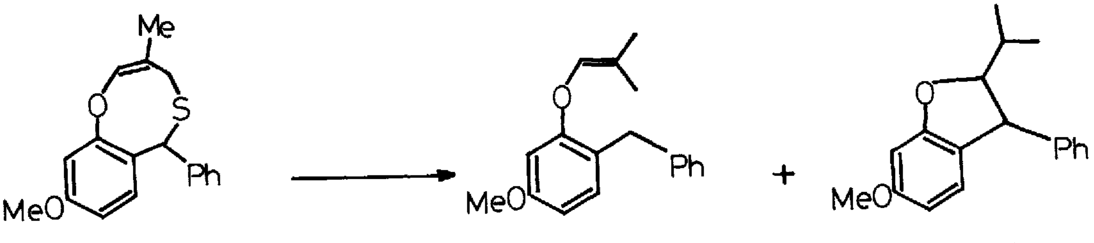

OH
R2
R1
Br
K2CO3
Ph
P4S10
△
S
chloramine-T
S=N–Ts
-S
N
Ts
O
N-Ts
S
≡
R2
Xylene
△

(3) (4) (5) (1) (6) (2) (7e) (5) (7)

Table 1. Synthesis of Thiones (5)

			(3)-(4)	(4)-(5)	(5)-(7)		
	R^1	R^2	Yield(%)	Yield(%)	Reaction time(hr)	Yield(%)	Property of 7
(7a)	H	H	94	43	0.5	100	green oil
(7b)	H	OMe	97	72	1.0	83	yellow oil
(7c)	Me	OMe	85	86	1.0	100	pale blue oil
(7d)	Cl	OMe	68	82	24.0	78	orange oil
(7e)	--	--	93	53	13.5	59	pale blue oil

Desulfurization of 7c with Raney nickel W-2 (room temp, over night) afforded the expected sulfur-free products 8c and 9c.[6] The result gives further evidence for the structure of 7 and also it is noteworthy that the dihydrobenzofuran derivative 9c was produced.



(7c) (8c) (9c)

It is considered that the thermal cyclization reaction of 5 proceeded in the manner of the intramolecular ene reaction involving the thiocarbonyl group as an enophile unit. There are few examples on the ene reaction of thiocarbonyl compounds. Intermolecular ene reaction is reported only for extremely reactive hexafluorothioacetone[7]. Internal thioaldehyde trapping by enes was reported by Vedejs et al. very recently,[8] but the mode of the reaction differs from that of the present case.[9] From these points of view, the present results seem to be very interesting and would provide a useful method for the preparation of unusual heterocycles (7).

References

1) E.M.Burgess and H.R.Penton,Jr,J.Org.Chem.,39,2885(1974);J.Am.Chem.Soc., 95,279(1973).
2) T.Saito and S.Motoki,J.Org.Chem.,44,2493(1979).
3) T.Saito, I.Oikawa and S.Motoki,Bull.Chem.Soc.Japan.,53,1023(1980).

4) T.Saito, N.Shibahara and S.Motoki,Tetrahedron Lett.,24,4435(1983).

5) Spectral data of 7b-e.

7b: IR(NaCl) 1650 cm^{-1}; MS m/e 284(M^{+}); ^{1}H-NMR(CDCl$_3$) δ 2.77(1H, dd, J=14.5, 9.5 Hz), 3.01(1H, ddd, J=14.5, 9.5, 1.2 Hz), 3.75(3H, s), 4.67(1H, ddd, J=9.5, 9.5, 7.5 Hz), 5.71(1H, s), 6.45(1H, dd, J=7.5, 1.2 Hz), 6.56(1H, d, J=2.4 Hz), 6.65(1H, dd, J=8.5, 2.4 Hz), 6.88(1H, d, J=8.5 Hz), 7.12 - 7.56(5H, m); ^{13}C-NMR(CDCl$_3$) δ 24.76(t), 44.98(d), 55.12(q), 101.13(d), 144.51(d).

7c: IR(NaCl) 1662 cm^{-1}; MS m/e 298(M^{+}); ^{1}H-NMR(CDCl$_3$) δ 1.66(3H, d, J=1.5 Hz), 2.63(1H, d, J=14.5 Hz), 3.14(1H, dd, J=14.5, 1.0 Hz), 3.73(3H, s), 5.55(1H, s), 6.34(1H, qd, J=1.5, 1.0 Hz), 6.52 - 6.64(1H, m), 6.76 - 6.91(1H, m), 7.00 - 7.58(6H, m); ^{13}C-NMR(CDCl$_3$) δ 19.50(q), 30.85(t), 46.64(d), 55.37(q), 123.94(s), 139.19(d).

7d: IR(NaCl) 1640 cm^{-1}; MS m/e 318(M^{+}); ^{1}H-NMR(CDCl$_3$) δ 3.10(1H, d, J=15.5 Hz), 3.33(1H, dd, J=15.5, 0.75 Hz), 3.75(3H, s), 5.56(1H, s), 6.52 - 7.56 (9H, m); ^{13}C-NMR(CDCl$_3$) δ 34.02(t), 46.30(q), 55.41(d), 123.36(s), 141.44(d).

7e: IR(NaCl) 1597 cm^{-1}; MS m/e 282(M^{+}); ^{1}H-NMR(CDCl$_3$) δ 2.12 - 2.70(2H, m), 2.76 - 3.32(2H, m), 3.91 - 4.60(2H, m), 5.40 - 5.72(2H, m), 5.89(1H, s), 6.76 - 7.82(9H, m). ^{13}C-NMR(CDCl$_3$) δ 25.88(t), 27.49(t), 41.13(d), 68.72(t), 123.21(d), 126.52(d).

6) 8c: colorless oil; yield 31 %; MS m/e 268(M^{+}); ^{1}H-NMR(CDCl$_3$) δ 1.63(3H, d, J=1.5 Hz), 1.66(3H, d, J=1.5 Hz), 3.75(3H, s), 3.93(2H, s), 6.12(1H, qq, J=1.5, 1.5 Hz), 6.44(1H, dd, J=9.1, 2.4 Hz), 6.46(1H, d, J=2.4 Hz), 6.98(1H, d, J=9.1 Hz), 7.19(5H, s); ^{13}C-NMR(CDCl$_3$) δ 15.11(q), 19.35(q), 35.43(t), 55.02(q), 117.46(s), 135.20(d).

9c: colorless oil; yield 39 %; MS m/e 268(M^{+}); ^{1}H-NMR(CDCl$_3$) δ 0.99(3H, d, J=7.0 Hz), 1.02(3H, d, J=6.7 Hz), 1.98(1H, qqd, J=7.0, 7.0, 5.5 Hz), 3.75(3H, s), 4.25(1H, d, J=7.0 Hz), 4.45(1H, dd, J=7.0, 5.5 Hz), 6.32(1H, dd, J=8.1, 2.4 Hz), 6.41(1H, d, J=2.4 Hz), 6.74(1H, d, J=8.1 Hz), 7.00 - 7.36(5H, m); ^{13}C-NMR(CDCl$_3$) δ 17.55(q), 18.37(q), 32.85(d), 51.32(d), 55.12(q), 95.57(d).

7) W.J.Middleton, E.G.Howard and W.H.Sharkey,J.Am.Chem.Soc.,83,2589(1961); J.Org.Chem.,30,1375,1384,1395(1965).

8) E.Vedejs, T.H.Eberlein and R.G.Wilde,J.Org.Chem.,53,2220(1988).

9) There are three different modes of intramolecular ene reaction in which the enophile is linked by either to the olefinic terminal (Type 1), the central atom (Type 2), or the allylic terminal (Type 3) of the ene unit. (W.Oppolzer and V.Snieckus,Angew.Chem.Int.Ed.,17,476(1978)). The present case belongs to the Type 3 reaction and the reaction reported by Vedejs is of the Type 2.

(Received in Japan 11 October 1988)