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NOVEL REACTIONS OF 1-BENZOYL-2-METHYL-3,4-DIHYDRO-2-THIANAPHTHALENE WITH COMPOUNDS HAVING AN ACIDIC HYDROGEN

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Summary: Thermal reaction of 1-benzoyl-2-methyl-3,4-dihydro-2-thianaphthalene(1) with acids or thiols in benzene afforded ring-opened products cleaving C_1-S bond. On the other hand, ring-expanded product was produced by the reaction of 1 with imides or phenols.

It is well-known that sulfur ylides are easily protonated by acids to form sulfonium salts. However, further reactions of the sulfonium salts have not been studied. Previously, we reported that a thermal reaction of benzoyl-stabilized cyclic sulfur ylides in alcohols was initiated by protonation of alcohols to a ylidic carbon followed by the nucleophlic attack of an alkoxide ion to a carbonyl carbon.[1)] The report attracted us to the possibility of extending the concept to other compounds having an acidic hydrogen atom.

We examined the reaction of 1-benzoyl-2-methyl-3,4-dihydro-2-thianaphthalene (1) with acids, thiols, phenols, and imides. In this communication, we wish to report very unique results that the sulfonium ion formed initially was attacked site-selectively by the counter anion to cause a new ring-opening reaction or a novel ring-expansion reaction.

Refluxing ylide 1 in benzene with 2eq. of acetic acid afforded o-(α-acetoxyphenacyl)phnethyl methyl sulfide(3) as a colorless oil in 89.0% yield: ^{1}H-NMR ($CDCl_3$) δ 2.12(3H,s,CH_3), 2.18(3H,s,$COCH_3$), 2.50-3.30(4H,m,CH_2×2), 7.10(1H,s,CH), 7.15-7.55(7H,m,ArH), 7.77-7.98(2H,m,ArH); IR (neat) ν max cm^{-1} 1700, 1745(CO); MS m/e 328(M^+). The sulfide 3 was produced by the reaction pathway that C_1-carbanion was protonated by acetic acid to form the sulfonium ion 2, which would be attacked on C_1-position by acetate anion and cleaved C_1-S bond. Under similar conditions, ylide 1 reacted with other acids and thiols to afford ring-opening products 4-9[3)] as shown in Table I.

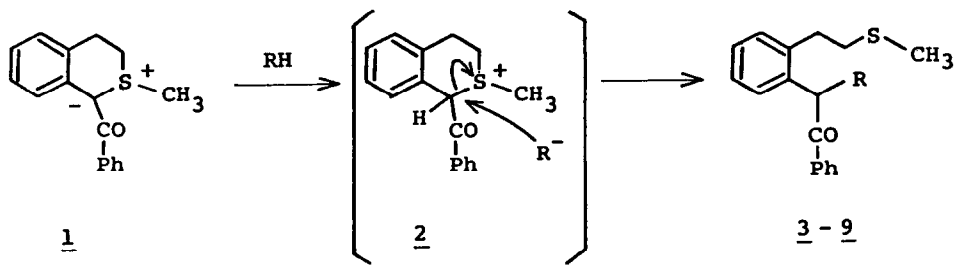

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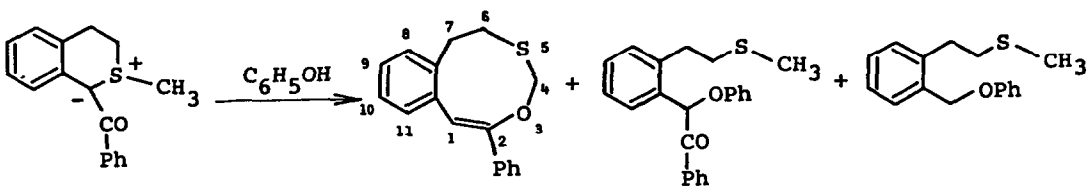
Table I: Thermal Reaction of Ylide 1 with Acids and Thiols

Acids and Thiols(RH)	Molar Ratio	Time(hr)	Product(Yield:%)
CH_3COOH	1eq.	7	3 (89.0)
C_6H_5COOH	10eq.	9	4 (81.8)
C_6H_5COSH	1eq.	2	5 (94.1)
o-HO-C_6H_4COOH	2eq.	18	6 (66.0)
o-H_2N-C_6H_4COOH	2eq.	17	7 (53.4)
C_6H_5SH	1eq.	23	8 (95.2)
$C_6H_5CH_2SH$	1eq.	25	9 (44.0)

Different from the reaction with alkoxide anions,[1] carboxylate or thiolate anions attacked on C_1 of the sulfonium ion 2. Therefore, we examined the reaction of 1 with phenol which is less acidic than carboxylic acids or thiols, and more acidic than alcohols.

Refluxing ylide 1 in benzene with 2eq. of phenol afforded ring-expanded product, 2-phenyl-6,7-dihydro-3,5-benzoxathionin(10)[4] as a colorless prisms: mp.107°; ^{1}H-NMR ($CDCl_3$) δ 2.74-3.30(4H,m,CH_2×2), 4.84(2H,s,CH_2), 6.45(1H,s,CH), 7.10-7.80 (9H,m,ArH); ^{13}C-NMR ($CDCl_3$) δ 32.234(C-7), 36.668(C-6), 72.316(C-4), 113.904(C-1), 139.611(C-2), 126.356, 126.722, 127.307, 128.500, 128.695, 129.233, 129.397(ArC); MS m/e 268(M^+). However, with 10eq. of phenol the ylide 1 afforded 10 and ring-opened products, 11 and 12[3] in 50.0%, 12.3%, and 19.8% yield, respectively. Further, with 100eq. of phenol the products 11 and 12 were obtained in 27.2% and 47.6% yield, respectively.

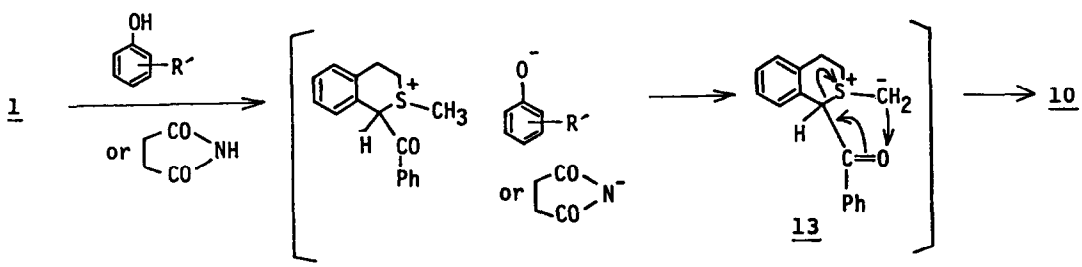


The probable mechanism for the formation of 10 involves the hydrogen abstraction of methyl group of sulfonium ion 2 by phenoxide ion followed by [2,3]sigmatropic rearrangement[5] of the methylide intermediate 13 to the nine-membered ring product 10. The result that the addition of phenol decreased 10 and increased 11 and 12 would be explained in the following way. Accompanied by the quantity of phenol, the ability of hydrogen abstraction from S-methyl group is decreased because of the intermolecular hydrogen bonding between phenoxide anion and excess phenol, and consequently, the nucleophilic attack of C_1 or a carbonyl carbon is increased. In the case of 100eq. of phenol, phenoxide anion formed the hydrogen

bond with phenol appears to attack the less crowded site, a carbonyl carbon, predominantly. In order to elucidate the influence of the substituents of phenols for the formation of 10, the reactions of 1 with 2eq. of several phenols were performed. The results showed that the phenols having a methyl or a methoxy group at the ortho position afforded 10 in high yield as shown in Table II.

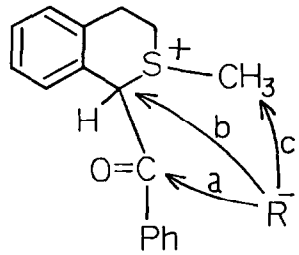
Table II: Thermal Reaction of Ylide 1 with Substituted Phenols

Phenols(R´)	Time(hr)	Product 10(Yield:%)
2-NO_2	43	21.3
2-CH_3	20	75.5
4-CH_3	37	52.7
2-OCH_3	39	83.2
4-OCH_3	60	49.3
2-NH_2	24	14.5
4-NH_2	22	13.1
2,4,6-CH_3	65	80.0



If a counter anion of 2 abstracted a hydrogen of the methyl group of 2 site-selectively, it is possible to synthsize only 10 from 1. We selected imides for the reaction because the conjugate base has poor nucleophilicity but the ability of hydrogen abstraction. The reaction of 1 with succinimide or phthalimide afforded only 10, as was expected, in 74.7% and 69.9% yield, respectively.

In conclusion, protonation on C_1-carbanion is the first step of the reaction of 1 with the compounds releasing a proton to form the sulfonium salt 2. The reaction sites of 2 are varied by the species of the counter anion. Namely, alkoxide anions attack a carbonyl carbon (path a)[1]; carboxylate or thiolate anions attack C_1 (path b); imidyl anions remove a hydrogen of the methyl group (path c). Further, phenoxide anion reacts to three sites (path a, b, and c) according to the quantity of phenol.



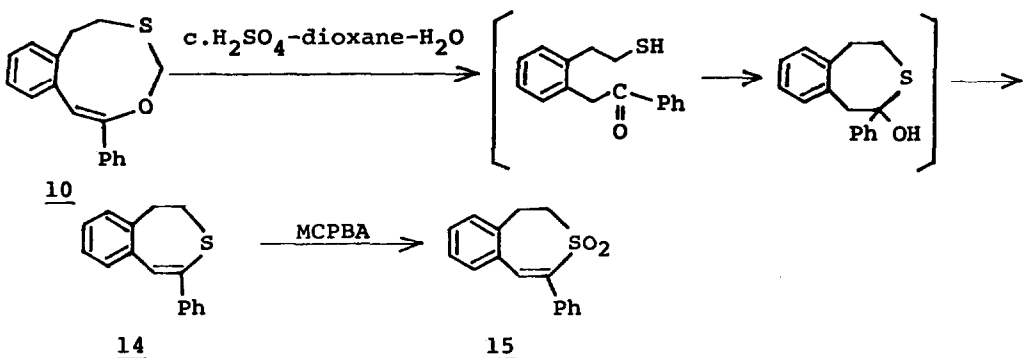
REFERENCES AND FOOTNOTES

1) M. Hori, T. Kataoka, H. Shimizu, and A. Tomoto, Tetrahedron Lett., 22, 3629 (1981).

2) Ylide 1 was stable in refluxing benzene.

3) All new compounds reported here had satisfactory analytical data.

4) The structure of 10 was also established chemically from the following hydrolysis and oxidation.



2-phenyl-4,5-dihydro-3-benzothiepin(14): ^{1}H-NMR ($CDCl_3$) δ 3.28(4H,s,CH_2×2), 6.82(1H,s,CH), 7.02-7.70(9H,m,ArH); MS m/e 238(M^+).

2-phenyl-4,5-dihydro-3-benzothiepin 3,3-dioxide(15): ^{1}H-NMR ($CDCl_3$) δ 3.25-3.70(4H,m,CH_2×2), 6.87(1H,s,CH), 7.15-8.00(9H,m,ArH); IR (KBr) ν max cm^{-1} 1120, 1289(SO_2); MS m/e 270(M^+); mp. 99-100°.

5) Non-base catalyzed [2,3]sigmatropic rearrangement of phenacyl sulfonium ylides were reported.

a) K. W. Ratts and A. N. Yao, J. Org. Chem., 33, 70 (1968).

b) A. Terabe and Y. Kishida, Chem. Pharm. Bull., 18, 505 (1970).

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