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SYNTHESES AND THERMAL REACTIONS OF 2-ALKYL(OR ARYL)-1-BENZOYL-3,4-DIHYDRO-2-THIANAPHTHALENES

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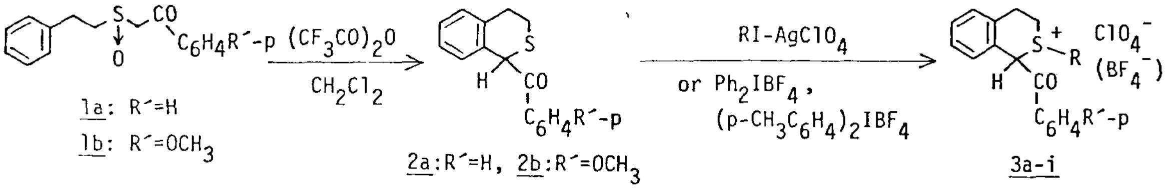
Summary: 1-Benzoyl-2-methyl-3,4-dihydro-2-thianaphthalene (4a) underwent novel intermolecular 1,4-rearrangement in refluxing toluene to give an enol ether 5a, while rearrangement of 2-phenyl derivative 4e proceeded intramolecularly in refluxing xylene to afford a 1,4-rearranged enol ether 5b. On the other hand, ylides 4a-e were refluxed in alcohols to afford some ring-opened products 10-12.

A large number of benzoyl-stabilized sulfur ylides have been synthesized and their reactivities have been investigated in past two decades. Thermal [2,3]sigmatropic rearrangement1) and Stevens-type 1,2-rearrangement2) of these ylides are well-known, however despite the facile enolization of the carbonyl group,3,4) the 1,4-rearrangement of S-substituent to the carbonyl oxygen atom has not been found. In this communication, we wish to report the syntheses of new benzoyl-stabilized cyclic sulfur ylides and their thermal reactions, especially a novel 1,4-rearrangement and ring-opening reactions.

Syntheses of 2-Alkyl(or Aryl)-1-benzoyl-3,4-dihydro-2-thianaphthalenes

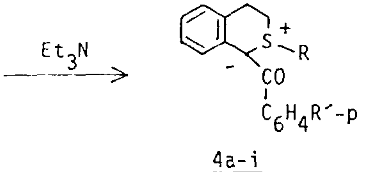
Phenacyl phenethyl sulfoxide (1a) was cyclized with trifluoroacetic anhydride in methylene chloride to give 1-benzoyl-2-thiochroman (2a).5) The Pummerer cyclization proceeded readily in comparison with that of methylsulfinylmethyl phenethyl ketone reported by Yonemitsu et al.6) and is very useful for the synthesis of sulfur heterocycles. Treatment with alkyl halides-silver perchlorate or diphenyliodonium tetrafluoroborate7) led 2a and 2b to the sulfonium salts 3a-i. The compounds 3a-i were deprotonated with triethylamine to give the corresponding ylides 4a-i.8)



1a: R´=H
1b: R´=OCH_3

2a:R´=H, 2b:R´=OCH_3

3a-i

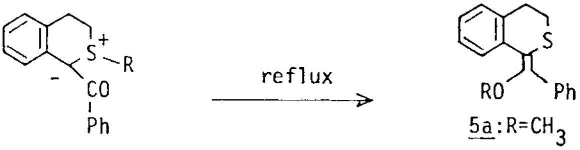


4a-i

Compd. 3, 4	R	R´	Compd. 3, 4	R	R´
a	CH_3	H	f	CD_3	H
b	C_2H_5	H	g	$p-CH_3C_6H_4$	H
c	$n-C_3H_7$	H	h	CH_3	OCH_3
d	$i-C_3H_7$	H	i	C_6H_5	OCH_3
e	C_6H_5	H			

Thermal 1,4-Rearrangement of 2-Alkyl(or Aryl)-1-benzoyl-3,4-dihydro-2-thianaphthalenes

Refluxing ylide 4a in dry toluene did not undergo the normal Stevens-type 1,2-rearrangement,[4,9] but did the 1,4-rearrangement to afford enol ether 5a as a yellow oil. The structure was characterized by its IR spectrum (no carbonyl absorption band) and its NMR spectrum [δ 3.46 (3H, s, OCH_3)]. Similarly in dry xylene, ylide 4e gave enol ether 5b[8,10] as colorless needles. However, ylides 4b-d were dealkylated to give 2a on refluxing in dry benzene or dry toluene.



4a-e

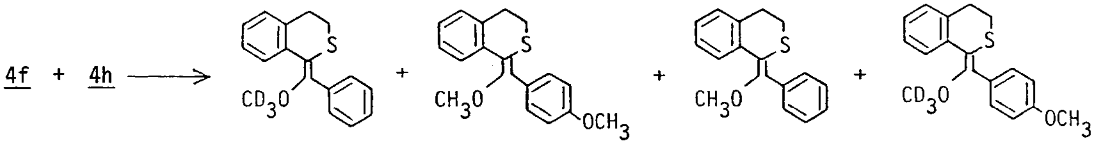
5a: R=CH_3

5b: R=C_6H_5

Table I: Thermal Rearrangement of 2-Alkyl(or Aryl)-1-benzoyl-3,4-dihydro-2-thianaphthalenes

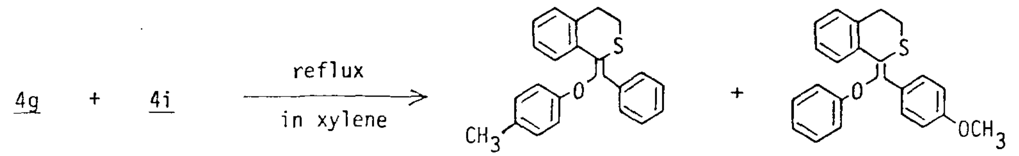
Compd.	Solvent (Time:hr)	Product (Yield:%)
4a	benzene (12)	4a (83.3)
	toluene (12)	5a (47.6)
4b	benzene (12)	2a (64.3)
	toluene (12)	2a (67.4)
4c	benzene (12)	2a (76.9)
	toluene (3)	2a (78.1)
4d	benzene (4)	2a (85.2)
	toluene (2)	2a (88.5)
4e	benzene (12)	4e (85.4)
	toluene (12)	4e (46.0), 5b (14.0)
	xylene (8)	5b (45.0)

In order to elucidate the mechanism of the novel 1,4-rearrangement of S-substituent to the carbonyl oxygen atom, crossover experiments were performed. For the methyl group migration a mixture of 1-benzoyl-2-trideuteriomethyl-3,4-dihydro-2-thianaphthalene (4f) and 1-(p-methoxybenzoyl)-2-methyl-3,4-dihydro-2-thianaphthalene (4h) was heated in dry toluene. Mass spectrum of the product showed four ion peaks at m/e 271, 298, 268, and 301, which were attributed to the molecular ion peaks of 5c, 5d, 5a, and 5e, respectively. This reaction produced two crossover products 5a and 5e, and therefore this rearrangement proceeded intermolecularly.



5c m/e 271 5d m/e 298 5a m/e 268 5e m/e 301

On the other hand, a crossover reaction using S-aryl ylides, 4g and 4i were carried out for the 1,4-rearrangement of the aryl group. Mass spectrum of the product exhibited two ion peaks at m/e 344 and 360, which were attributed to the molecular ion peaks of 5f and 5g, respectively. The product did not contain crossover products and therefore this reaction is an intramolecular rearrangement.

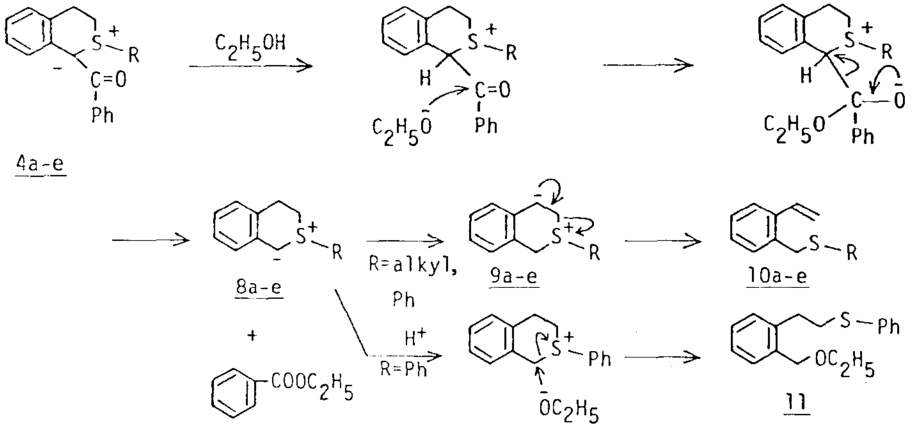


5f m/e 344 5g m/e 360

The differences of thermal rearrangements between ylides 4a and 1-benzoyl-2-methyl-2-thianaphthalene (6) can be explained by the stereochemical consideration on the rearranged products. 1,2-Shift of the methyl group of 4a was prohibited by steric hindrance between an axial C_4-H and an axial C_1-methyl group, or between C_8-H and an equatorial C_1-methyl group in 1-benzoyl-1-methyl-2-thiochroman. Consequently the methyl group rearranged to the carbonyl oxygen atom. Steric crowdness between C_4-H and the C_1-methyl group was reduced in 1-benzoyl-1-methyl-2-thiochromene (7), and therefore the substituent on sulfur atom of 6 migrated to the C_1-position.

Thermal Reactions of 2-Alkyl(or Aryl)-1-benzoyl-3,4-dihydro-2-thianaphthalenes

Refluxing ylide 4a in ethanol afforded methyl o-vinylbenzyl sulfide (10a) as a yellow oil together with ethyl benzoate. The structure of 10a was elucidated by its NMR spectrum: δ 1.94 (3H, s, CH_3), 3.67(2H, s, CH_2), 5.28(1H, dd, J=1.4, 11.1Hz, olefinic H), 5.63(1H, dd, J=1.4, 17.4 Hz, olefinic H), 7.09(1H, dd, J=11.1, 17.4Hz, olefinic H) and high-resolution MS: m/e 164.0634 (Calcd for $C_{10}H_{12}S$, 164.0632). The sulfide 10a was identified by comparing with the authentic sample prepared by treating dimethyl sulfoxide with o-vinylphenylmagnesium chloride. Under similar conditions, ylides 4b-d gave 10b-d, respectively. Similar treatment of ylides 4a-d with methanol gave sulfides 10a-d and methyl benzoate. The ylides 4a-d would be protonated in ethanol to form the corresponding sulfonium salts, which would be attacked by ethoxide anion to afford eventually the ylide intermediate 8a-d and ethyl benzoate. Ylides 8a-d isomerized to 9a-d, which underwent α´,β-elimlnation to give sulfides 10a-d. On the other hand, refluxing ylide 4e in ethanol afforded phenyl o-vinylbenzyl sulfide (10e), ethyl benzoate, and o-(ethoxymethyl)phenethyl phenyl sulfide (11) as a colorless oil: NMR($CDCl_3$) δ 1.19(3H, t, J=7.2Hz, CH_3), 2.90-3.25(4H, m, CH_2×2), 3.49(2H, q, J=7.2Hz, CH_2), 4.43(2H, s, CH_2), 7.10-7.53(9H, m, ArH); high-resolution MS m/e 272.1242 (Calcd for $C_{17}H_{20}OS$, 272.1242). The sulfide 10e is considered to be produced via the



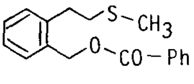
Compd.	R
a	CH_3
b	C_2H_5
c	n-C_3H_7
d	i-C_3H_7
e	C_6H_5

same route as that for 10a, while 11 was formed by the protonation on C_1-position of the ylide intermediate 8e, the subsequent attack of ethoxide anion on C_1-position and the cleavage of C-S bond.[11] When the ylide 4a was refluxed in t-butanol, o-(methylthioethyl)benzyl benzoate (12) was formed as a colorless oil: NMR($CDCl_3$) δ 2.08(3H, s, CH_3), 2.55-3.35(4H, m, CH_2×2), 5.40(2H, s, CH_2), 7.20-7.60(7H, m, ArH); IR(neat) ν max cm^{-1} 1715(C=O); high-resolution MS m/e 286.1008 (Calcd for $C_{17}H_{18}O_2S$, 286.1010). This result shows that the approach of t-butoxide anion to a carbonyl carbon atom was hindered because of its bulkiness, and therefore the attack of water contained in t-butanol prevailed.

Synthetic application of the reaction is under investigation.

Table II: Thermal Reactions of 2-Alkyl(or Aryl)-1-benzoyl-3,4-dihydro-2-thianaphthalenes

Compd.	Solvent (Time: hr)	Product (Yield: %)
4a	ethanol (3)	10a (85.4)
4b	ethanol (3)	10b (83.9)
4c	ethanol (3)	10c (80.1)
4d	ethanol (3)	10d (69.8), 2a (10.5)
4e	ethanol (8)	10e (67.2), 11 (12.1)
4a	methanol (3)	10a (80.0)
4a	t-butanol (28)	12 (44.0)



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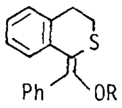
8) All new compounds reported here had satisfactory analytical data.
9) Under similar conditions, 2-alkyl-1-benzoyl-2-thianaphthalenes gave 1-alkyl-1-benzoyl-2-thiochromenes together with 1-benzoyl-2-thiochromene.
10) Enol ether 5 is more stable than 5´ because of the steric hindrance between C_8-H and $C_{2'}$-H.
11) 1,2-Diphenyl-2-thiochromenium perchlorate was ring-opened similarly. M.Hori, T. Kataoka, H. Shimizu, and S. Sugai, Chem. Pharm. Bull. (Tokyo), 22, 2752 (1974).



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