Sommelet-Hauser Rearrangement of Oxygen and Sulfur Containing Heteroaromatic Sulfonium Ylides

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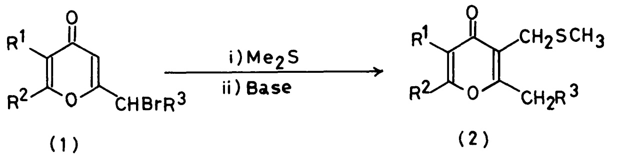
Synopsis. A Sommelet-Hauser rearrangement of sulfonium ylides of 4*H*-pyran-4-ones, furan, and thiophenes are discussed. The sulfonium halides which were prepared from excess dimethyl sulfide with corresponding halides were treated with NaH or NaOR in a polar solvent to give moderate to good yields of rearranged products.

Allyl and arylsulfonium ylides undergo an orbital-symmetry allowed [2.3] sigmatropic rearrangement, commonly known as the Sommelet-Hauser rearrangement.[1] The Sommelet-Hauser rearrangement of acyclic sulfonium ylides[1] and its aromatic analogues[2] can be widely quoted. However, the rearrangement of heteroaromatic ylides has been sparsely reported.[3]

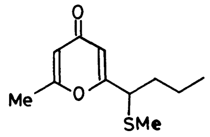
We wish to report here on the Sommelet-Hauser rearrangement of 4-pyranones, furan and thiophene derivatives. Many methods for the preparation of a sulfonium ylide are known, such as sulfonium salt-base,[4] carbene insertion,[5] and nitrene addition.[6] We prepared the sulfonium ylides via the sulfonium salt-base, which we found to be a simple method.

In general, a Sommelet-Hauser rearrangements of heteroaromatic compounds were carried out by treating the substrates in an inert atmosphere with an excess of dimethyl sulfide, followed by treatment with a base (MeONa-MeOH, EtONa-EtOH, or NaH). Following this procedure, 2,6-dimethyl-3-methylthiomethyl-4*H*-pyran-4-one (**2a**) was obtained in 92% yield from 2-bromomethyl-6-methyl-4*H*-pyran-4-one (**1a**).[7] In this reaction none of the [1.2] rearranged product was detected. Compound **2a** was also prepared by treating the sulfonium salt of **1a** with sodium hydride in refluxing THF or dioxane in 84 and 55% yields, respectively.



(1) (2)

a: $R^1=R^3=H, R^2=Me$
b: $R^1=R^3=H, R^2=Ph$
c: $R^1=OCH_2Ph, R^2=R^3=H$
d: $R^1=H, R^2=Me, R^3=CH_2CH_2CH_3$



(3)

The halopyrans, **1b** and **1c**, gave the corresponding rerranged products, **2b** and **2c**, in 87 and 73% yields, respectively. In contrast, a treatment of the branched bromide **1d** gave only 3% of the desired product **2d**, together with 52% of 2-methyl-6-(1-methylthiomethyl)-4*H*-pyran-4-one (**3**).

2-(Chloromethyl)furan (**4**) gave **5** in 34% yield. However, the sulfonium salt of **4** and the rearranged product **5** were unstable and easily decomposed to a black tar.

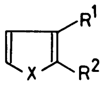
3-(Bromomethyl)thiophene (**6**) afforded rearranged product **7** in 67% yield. Compound **7** was also

Table 1. Spectral Data of the Rearranged Products

Compound	IR/cm^{-1}	^{1}H NMR (δ)			MS	
		S-CH$_3$	C$_2$-CH$_3$	C$_3$-CH$_2$-S	Found (*m/z*)	Calcd (M)
2a	1670 1600 1185	2.19	2.29	3.38	C; 58.60% H; 6.52	58.68%[a)] 6.56
2b	1650 1615 1170	2.18	2.50	3.63	246.3240	246.3246 ($C_{14}H_{14}O_2S$)
2c	1635 1615 1185	2.07	2.17	3.37	276.3500	276.3514 ($C_{15}H_{16}O_3S$)
5	1625 1515 1180	1.92	2.23	3.37	142.0451	142.0451 ($C_7H_{10}OS$)
7	3100 1250	2.00	2.20	3.73	158.0224	158.0244 ($C_7H_{10}S_2$)
11	1680 1470	1.88	2.43	3.72	208.0739	208.0739 ($C_{11}H_{12}S_2$)

a) Elemental analysis data was listed for compound **2a**.

obtained in 60% yield when the sulfonium bromide of **6** was treated with sodium ethoxide in ethanol at room temperature and in 22% yield when the same reaction was carried out at 0 °C. Interestingly, the reaction in refluxing ethanol gave 24% of the ethyl ether **8** in addition to 12% of **7**. A similar result was obtained in the case of sodium methoxide in refluxing methanol (**7**: 19%, **9**: 19%). The mechanisms for the formation of **8** and **9** are sitll not clear.



(4): R^1=H, R^2=CH_2Cl, X=O

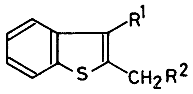
(5): R^1=CH_2SCH_3, R^2=CH_3, X=O

(6): R^1=CH_2Br, R^2=H, X=S

(7): R^1=CH_3, R^2=CH_2SCH_3, X=S

(8): R^1=$CH_2OCH_2CH_3$, R^2=CH_2SCH_3, X=S

(9): R^1=CH_2OCH_3, R^2=CH_2SCH_3, X=S



(10): R^1=H, R^2=Br

(11): R^1=CH_2SCH_3, R^2=H

The sulfonium bromide of 2-(bromomethyl)benzo[*b*]thiophene (**10**)[8] gave the desired product **11** in 57% yield.

We have thus demonstrated that the heteroaromatic ylides undergo an efficient Sommelet–Hauser rearrangement. Moreover, the methylene of a newly formed methylthiomethyl group can be used as a d^1-synthon. Applications of the aforementioned synthetic potentialities of this reaction are presently being studied in the laboratory. Results will be communicated separately.

Experimental

2,6-Dimethyl-3-methylthiomethyl-4*H*-pyran-4-one (2a): A mixture of **1a** (2.03 g, 10 mmol) in 5 ml of chloroform and excess dimethyl sulfide (3.72 g, 60 mmol) was stirred overnight at room temperture under nitrogen. The resulting precipitate was collected by filtration and, without further purification, the precipitate was added to an equimolar amount of sodium methoxide in 20 ml of methanol. The mixture was heated to reflux for 2 h, cooled, neutralized with diluted hydrochloric acid and worked up as usual to give a crude product which was purified by silica-gel column chromatography using benzene–ethyl acetate (2:1) as an eluent to give colorless plates of **2a** (1.69 g, 92%), mp 56—58 °C (from benzene–hexane=1:3).

Sulfonium bromide of **1a** (1.02 g, 5 mmol) was treated with sodium hydride (132 mg, 5.5 mmol) in refluxing THF (15 ml) or in refluxing dioxane (12 ml) for 2 h under nitrogen to give **2a** in 773 mg (84%) or 506 mg (55%), respectively. Similarly, rearranged products **2b** (87%; mp 77—78 °C), and **2c** (73%; pale yellow liquid) were obtained. Spectral data are listed in Table 1.

Attempted Rearrangement of the Branched Sulfonium Ylide: A mixture of **1d** (2.31 g, 9.43 mmol) prepared from 2-butyl-6-methyl-4*H*-pyran-4-one[9] and excess dimethyl sulfide (1.84 g, 13.0 mmol) in chloroform (8 ml) was treated according to the procedure mentioned above; the products were purified similarly to give **2d** (52 mg, 3%) and **3** (975 mg, 52%). ^{1}H NMR of **2d** (CCl_4, δ): 0.92 (t, 3H), 1.20—1.87 (m, 4H), 2.00 (s, 3H), 2.25 (s, 3H), 2.60 (t, 2H), 3.60 (s, 2H) and 5.40 (s, 1H). ^{1}H NMR of **3** ($CDCl_3$, δ): 0.97 (t, 3H), 1.10—1.80 (m, 4H), 2.00 (s, 3H), 2.25 (s, 3H), 3.34 (t, 1H) and 5.90 (s, 2H). MS of **3**: Found: *m/z* 212.0876, Calcd as $C_{11}H_{16}O_2S$: M, 212.0870. *m/z* 212 (M^+, 100), 141 (33), 85 (90) and 43 (60).

3-Methylthiomethyl-2-methylfuran (5): A mixture of 2-(chloromethyl)furan (**4**; 816 mg, 7.0 mmol) and dimethyl sulfide (1.28 g, 21 mmol) was kept at room temperature overnight. The resulting brown paste was stirred with sodium ethoxide (7.7 mmol) in ethanol (40 ml) at 0 °C for 3.5 h. The reaction mixture was quenched with water (12 ml), extracted with ether, dried over anhydrous magnesium sulfate, concentrated, and purified by silica-gel column chromatography with hexane to give **5** (338 mg, 34%) as a colorless oil. The spectral data are listed in Table 1.

3-Methyl-2-(methylthiomethyl)thiophene (7): 3-(Bromomethyl)thiophene (**6**; 1.04 g, 5.9 mmol), which was prepared from 3-methylthiphene with NBS and benzoyl peroxide in refluxing benzene,[7] was mixed with dimethyl sulfide (733 mg, 11.8 mmol) the mixture was kept overnight at room temperature. The resulting brown paste was washed several times with ether and dried to give a crude sulfonium bromide (959 mg, 68%). This sulfonium bromide in THF (25 ml) was treated with sodium hydride (106 mg, 4.4 mmol) with stirring at room temperature for 22 h. The reaction mixture was quenched with water, extracted with ether, dried, concentrated and purified by silica-gel column chromatography with hexane to give **7** (628 mg, 67%) as a colorless oil. The sulfonium bromide of **6** (720 mg) was treated with sodium ethoxide in refluxing ethanol (20 ml) for 2 h to give **7** (57 mg, 12%) and 3-ethoxymethyl-2-(methylthiomethyl)thiophene (**8**; 146 mg, 24%). IR (neat) of **8**: 3100, 2990, and 1090 cm^{-1}. ^{1}H NMR (CCl_4, δ) of **8**: 1.20 (t, 3H, J=7.0 Hz), 2.04 (s, 3H), 3.45 (q, 2H, J=7.0 Hz), 3.82 (s, 2H), 4.41 (s, 2H), 6.88 (d, 1H, J=5.2 Hz) and 7.07 (d, 1H, J=5.2 Hz). MS of **8**: Found: *m/z* 202.0474, Calcd as $C_9H_{14}OS_2$: M, 202.0474. ^{13}C NMR ($CDCl_3$, δ) of **8**: 14.96 (q), 15.45 (q), 30.27 (t), 65.64 (t), 65.74 (t), 123.3 (d), 128.8 (d), 136.2 (s), and 138.4 (s).

The sulfonium bromide of **6** (720 mg) was also treated with sodium methoxide in refluxing methanol (20 ml) for 2 h to give **7** (90 mg, 19%) and 3-methoxymethyl-2-(methylthiomethyl)thiophene (**9**; 108 mg, 19%). ^{1}H NMR (CCl_4, δ) of **9**: 2.04 (s, 3H), 3.30 (s, 3H), 3.82 (s, 2H), 4.38 (s, 2H), 6.88 (d, 1H, J=5.0 Hz) and 7.08 (d, 1H, J=5.0 Hz).

2-Methyl-3-(methylthiomethyl)benzo[*b*]thiophene (11): A solution of 2-(bromomethyl)benzo[*b*]thiophene (**10**)[8] (2.37 g, 10.4 mmol) in chloroform (1 ml) was added to dimethyl sulfide (1.97 g, 31.7 mmol); the mixture was kept overnight at room temperature. The resulting white precipitate was filtered, washed several times with ether, dried to give crude sufonum bromide of mp 132—133 °C (2.45 g, 81%). To a solution of this sulfonium bromide (941 mg, 3.33 mmol) in THF (15 ml) was added sodium hydride (184 mg, 3.5 mmol) the mixture was heated to reflux for 5 h. The reaction mixture was quenched with 1 M-hydrochloric acid (1M=1 mol dm^{-3}), extracted with benzene, dried, concentrated and purified by silica-gel column chromatography with benzene–ethyl acetate (9:1) to give **11** (365 mg, 57%) as yelow paste. Spectral data are listed in Table 1.

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