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The Formation of Two Kinds of Thiophene Derivatives by the Reaction of the 4*H*-Pyran-4-thione Derivative with Dimethyloxosulfonium Methylide in a One-pot Process

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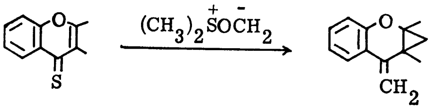
Synopsis. The reaction of 2,6-dimethyl-3,5-diphenyl-4*H*-pyran-4-thione with dimethyloxosulfonium methylide occurred facilely to give two kinds of 2-thienylacetones, accompanied by a five-membered α,β-unsaturated thione, a naphtho[2,1-*b*]thiophene derivative, and a hemithioacetal.

In our previous report, the reaction of the 4*H*-1-benzopyran-4-thione (chromothione) derivatives with dimethyloxosulfonium methylide (DOSM) was reported to give 3,4-benzo-5-methylene-2-oxabicyclo[4.1.0]hept-3-enes (vinylcyclopropanes), with the increment of two methylene groups, accompanied by the removal of the sulfur in a one-pot procedure, although there have been few reports on the addition of DOSM to thioketones.[1] There is, thus, interest in the study of the behavior of DOSM toward the parent 4*H*-pyran-4-thione derivative, **1**, in comparison with the benzo-condensed chromothione system.



Experimental

The mps are uncorrected. The IR and the UV spectra were measured with Hitachi 215 and 124 model apparatuses respectively. The ^1H-NMR spectra were measured on a Varian T-60 spectrometer in $CDCl_3$, using tetramethylsilane as the internal standard. We are indebted to Drs. Shizuko Eguchi and Yasuhito Uchio, Hiroshima Univ., for obtaining the mass and the ^{13}C-NMR spectra respectively.

Preparation of Thione 1. The treatment of 2,6-dimethyl-3,5-diphenyl-4*H*-pyran-4-one[2] with P_2S_5 in 1,2-dichloroethane under reflux for 2 h afforded pinkish prisms. Mp 224—226 °C (80% yield, from 2-propanol) (see Table 1).

*Reaction of 4*H*-Pyran-4-thione 1 with DOSM.* To DOSM in dimethyl sulfoxide (15 ml), prepared from NaH (66% in oil, 130 mg, 3.57 mmol) and trimethyloxosulfonium iodide (850 mg, 3.86 mmol), dry ether (5 ml) and **1** (500 mg, 1.71 mmol) were added, after which the mixture was stirred at room temperature for several minutes under a nitrogen atmosphere. After the usual work-up process, the crude product was purified by the use of a silica-gel column, followed by preparative TLC using ether-light petroleum as the eluent, to give five products (see Table 1): **2**, violet oil (15 mg, 3%, λ_{max} 355 nm (log ε 3.42), unstable; a facile isomerization occurred to give **3** quantitatively); **3**, colorless oil (80 mg, 15%; monooxime, mp 180—182 °C from methanol–water); **4**, mp 40—42 °C (38 mg, 7%, from light petroleum); **5**, mp 117—119 °C (trace, from light petroleum, λ_{max} 243 (4.58), 285 (3.92), 315 (3.28), 329 nm (3.41)); **6**, mp 110—112 °C (110 mg, 19%, from light petroleum, λ_{max} 297 nm (3.47); monoacetate, *m*/*e* 380 (M^+), 338, 205 (base), calcd for $C_{23}H_{24}O_3S$ (Mw 380); δ 7.58—7.13 (10H, m), 3.80 (2H, s, methylene), 2.10 (3H, s), 2.02 (3H, s), 1.98 (3H, s), 1.92 (3H, s)).

Results and Discussion

The treatment of **1** with DOSM in dimethyl sulfoxide (DMSO) afforded five products, **2**, **3**, **4**, **5**, and **6**, whose structures were assigned to a five-membered α,β-unsaturated thione, two kinds of thienylacetones, a naphthothiophene, and a hemithioacetal, respectively, on the basis of their microanalyses and spectral data, as shown in the table (see also Experimental section). The production of two kinds of 2-thienylacetone derivatives, **a**, was expected by comparing the spectral characteristics of **3** and **4** with those of the related 2-furylacetones.[3] The UV spectrum of **5** agreed well with the parent naphtho[2,1-*b*]thiophene reported in the literature.[4] Therefore, it is noteworthy that all these compounds in our present work contain sulfur, while vinylcyclopropanes have been obtained by the reaction of chromothione with DOSM.[1]

Now let us discuss the structural problem of two kinds of thiophene derivatives, **3** and **4**. As it has been reported that the acid-catalyzed deuterium exchange of α-hydrogen on the thiophene ring took place 10^3 times as fast as that of β-hydrogen,[5] **3** and **4** were subjected to deuterium exchange in acetic acid-d_4 at 140 °C for 1.5 h; it was found that a vinyl signal (δ=6.87 in **3**) completely disappeared, while, on the contrary, another signal (δ=6.65 in **4**) appeared sufficiently in the ^1H-NMR spectra. Accordingly, **3** possesses α-hydrogen on the thiophene ring, while there is no such hydrogen in **4**.

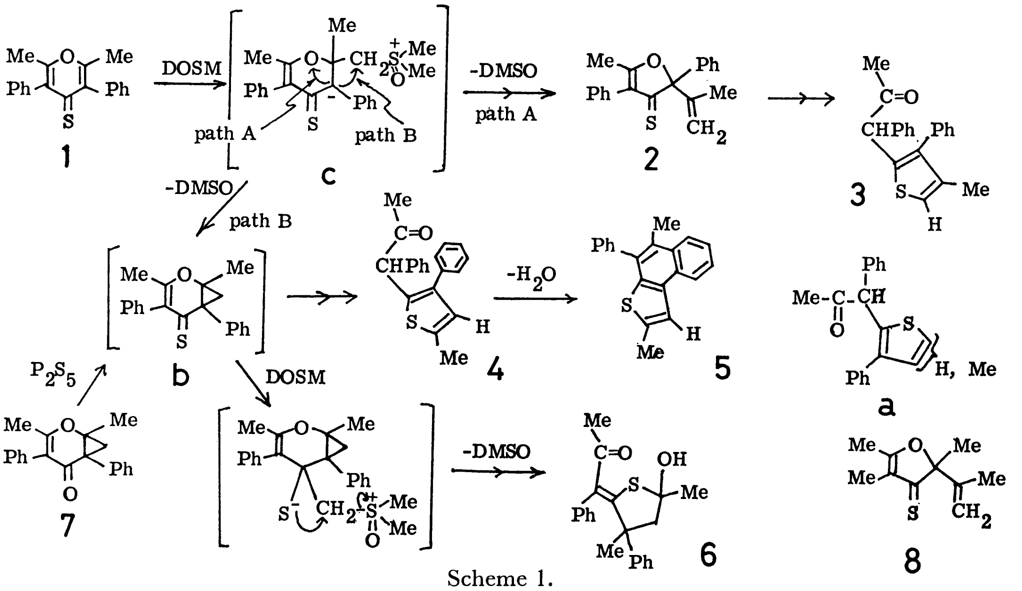
Compound **2** rearranged facilely into **3** quantitatively under neat conditions. Ketone, **7**,[3] was treated with P_2S_5 in carbon tetrachloride at room temperature for 6 h to give **4**, but **3** could not be detected. It may, therefore, be expected that there are two kinds of formation routes, where **3** and **4** are derived from a five-membered thione, **2** (Path A), and a six-membered one, **b** (Path B), *via* the Michael adduct, **c**, at the first stage; nonetheless, there is a high reactivity of the thiocarbonyl group at the C-4 position of **1**. One of the plausible pathways for understanding the production of these materials is presented in the Scheme 1.

It is interesting that **2** was isolated as the sole product (30%) from **1** and DOSM, concomitant with the recovery of **1**, when DMSO was diluted with tetrahydrofuran (THF) (1:2 v/v) at 0 °C for 30 min; this is probably because of the stabilization of the intermediate desirable for five-membered α,β-unsaturated thione formation.

Table 1. The IR, NMR, mass, and elemental analyses data

Compound	IR ν_{max} (cm^{-1})	^{1}H-NMR δ (ppm) in $CDCl_3$	Mass (*m/e*)	Found (Calcd) % C	H	S	Formula
1	1630, 1240, 870, 750	7.50—7.05 (10H, m), 2.30 (6H, s)	292 (M$^+$)	77.79 (78.05)	5.53 (5.52)	11.09 (10.97)	$C_{19}H_{16}OS$
2	1585, 1495, 1250, 975	7.77—7.20 (10H, m), 5.20 (2H, broad s)[a] 2.37 (3H, s), 1.83 (3H, s)	306 (M$^+$) 288, 205[c]		b)		$C_{20}H_{18}OS$
3*	1715, 1600	7.47—6.93 (10H, m), 6.87 (1H, s), 5.07 (1H, s, methine), 2.0 (6H, s)	306 (M$^+$) 277, 263[c]	74.37[d] (74.73)	5.97[d] (5.96)	4.34[d,e] (4.36)[e]	$C_{20}H_{18}OS$ ($C_{20}H_{19}NOS$)[d]
4*	1715	7.25 (10H, s), 6.65 (1H, s), 5.28 (1H, s, methine), 2.43 (3H, s), 2.08 (3H, s)	306 (M$^+$) 279, 263	78.39 (78.01)	5.92 (6.20)	10.46 (9.99)	$C_{20}H_{18}OS$
5	1440, 900, 730, 690	8.10—7.87 (1H, m), 7.70—7.5 (1H, m), 7.47—7.07 (7H, m), 7.02 (1H, s, vinyl), 2.85 (3H, broad s), 2.22 (3H, s)	288 (M$^+$)[c] 272, 246	83.00 (83.29)	5.81 (5.59)	9.98 (11.12)	$C_{20}H_{16}S$
6*	3500, 1670, 1490, 940, 750	7.92—7.63 (2H, m), 7.53—7.10 (8H, m), 5.02 (OH), 3.50 (1H, d)[f] [7.0],[g] 2.67 (1H, d)[f] [3.2], 2.37 (3H, s) [2.3], 1.92 (3H, s) [1.2], 0.80 (3H, s) [4.0]	338 (M$^+$) 295, 205[c]	74.52 (74.55)	6.55 (6.67)	9.48 (9.45)	$C_{21}H_{22}O_2S$

* ^{13}C-NMR ($CDCl_3$) δ: **3**, 205.1 (s), 141.3, 138.2, 137.1, 136.7, 130.6, 129.8, 129.4, 128.8, 128.5, 128.1, 127.9, 127.5, 120.3 (d), 58.9 (d), 29.2 (q), 15.4 (q). **4**, 205.1 (s), 140.6, 138.8, 138.5, 136.8, 133.1, 128.7, 128.5, 127.9, 127.4, 127.2, 58.3 (d), 29.0 (q), 15.0 (q). **6**, 211.8 (s), 149.0 (s), 137.2 (s), 136.7 (s), 130.4, 128.6, 128.5, 128.3, 127.3, 81.9 (s), 78.7 (s), 51.7 (t), 30.0 (q), 26.4 (q), 18.4 (q). a) It was separated to δ 5.42 and 5.17 in C_6D_6. b) Too unstable to obtain an analytically pure sample. c) Base peak. d) Monooxime. e) Nitrogen. f) J=16 Hz. g) Downfield shifts (δ, ppm) caused by the addition of Eu(fod)$_3$ (1 equiv.) are shown in brackets.



Scheme 1.

The reaction of DOSM to 2,3,5,6-tetramethyl-4*H*-pyran-4-thione in DMSO did not afford any vinylcyclopropanes, but only complicated mixtures difficult to identify, when THF–DMSO was used as the solvent, a five-membered unsaturated thione, **8**, could be isolated in a 5% yield: λ_{max} 345 nm; $\delta(CCl_4)$ 4.98 (1H, s), 4.83 (1H, s), 2.20 (3H, s), 1.82 (3H, s), 1.55 (6H, s); *m/e* 182 (M$^+$), 167, 139.[6)]

In summary, the reactivity of 4*H*-pyran-4-thiones to DOSM is found to be quite different from that of the corresponding benzo-condensed reactants.

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