## INTRAMOLECULAR MICHAEL AND ANTI-MICHAEL ADDITIONS OF THIOLATE TO CONJUGATED ACETYLENIC KETONES

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Abstract. The reaction of acetylenic ketones  $\underline{1}$  with carbon disulfide in the basic system sodium hydride/dimethylformamide and subsequent intramolecular cyclization to 4H-thiopyran-4-ones  $\underline{3}$  and  $\underline{3}(2H)$ -thiophenones  $\underline{4}$  are reported.

For some time we have been interested in intramolecular additions of sulfur nucleophiles to C,C double<sup>1</sup> or C,C triple bonds<sup>2</sup> as precursors to a variety of sulfur heterocycles. The reactions appear to have considerable synthetic potential. As a further versatile route to these compounds, we studied the reaction of methyl phenylethynyl ketone <u>1a</u> and ethyl phenylethynyl ketone <u>1b</u> with carbon disulfide in the basic system sodium hydride/ dimethylformamide. As shown in Scheme 1, the primarily formed but not isolated monosodium salt <u>2</u> leads by intramolecular nucleophilic addition and alkylation to a mixture of Michael and anti-Michael products <u>3</u> and <u>4</u>, respectively. All reactions were carried out at room temperature. The formation of <u>4a-d</u> provides additional exceptions<sup>3-5</sup> to the usual expectation<sup>6</sup> that  $\alpha$ ,  $\beta$ -unsaturated carbonyl systems do not add nucleophiles at  $C_{\alpha}$ . In the mixture obtained from <u>2</u> Michael adduct <u>3</u> was in considerable excess over its anti-Michael addition product <u>4</u> (ca. 4:1 mixture, determined by <sup>1</sup>H NMR).<sup>7</sup>

In the nucleophilic addition on a conjugated acetylenic ketone at  $C_{\beta}$  an energetically unfavorable geometry of an allenic enolate within a sixmembered ring would be required. The fact that the reactions took a course mainly to a six-membered ring is in accordance with the recently proposed stereoelectronically controlled pathway for similar intramolecular processes. On the other hand the formation of some anti-Michael isomer <u>4</u> by addition at  $C_{\alpha}$  indicates that a phenyl ring is indeed capable of stabilizing a developing anion.

The structures are consistent with spectroscopic data.<sup>9</sup> Whereas the expected carbonyl stretching vibration for  $\alpha$ ,  $\beta$ -unsaturated ketones is found in the region at 1645-1655 cm<sup>-1</sup> for compounds <u>4</u> it is shifted in the isomeric thiopyranones <u>3</u> to 1600-1605 cm<sup>-1</sup>.

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Scheme 1

No.	R	R'	Yield [%]	mp [°C]	<sup>1</sup> H NMR (CDCl <sub>3</sub> /HMDS int.) <sup>a)</sup> [ppm]
<u>38</u>	Н	сн <sub>3</sub>	55	72-74	2.57 (s, SCH <sub>3</sub> ); 6.83 (d, -CH=); 7.01 (d, -CH=, <sup>4</sup> J=1.22 Hz); 7.31-7.60 (m, 5H arom)
<u>3b</u>	Η	° <sub>6</sub> <sup>H</sup> 5−CH <sub>2</sub>	46	87-88	4.23 (s, SCH <sub>2</sub> ); 6.94 (d, -CH=); 7.02 (d, -CH=, <sup>4</sup> J=1.22 Hz); 7.30-7.52 (m, 10H arom)
<u>30</u>	Н	$p-Br-C_6H_4-CH_2$	72	91–92	4.16 (s, SCH <sub>2</sub> ); 6.92 (d, -CH=); 7.01 (d, -CH=, <sup>4</sup> J=1.20 Hz); 7.16-7.54 (m, 9H arom)
<u>3đ</u>	CH3	CH3	43	81-82	2.24 (s, CH <sub>3</sub> ); 2.59 (s, SCH <sub>3</sub> ); 7.10 (s, -CH=); 7.25-7.55 (m, 5H arom)
<u>4a</u>	Н	сн <sub>3</sub>	13	135-136	2.60 (s, SCH <sub>3</sub> ); 6.18 (s, -CH≈); 7.39-7.59 (m, 5H arom); 7.62 (s, -CH≈)
<u>4b</u>	Η	с <sub>6</sub> н <sub>5</sub> -сн <sub>2</sub>	11	104–105	4.45 (s, SCH <sub>2</sub> ); 6.28 (s, -CH≈); 7.20-7.60 (m, 10H arom); 7.63 (s, -CH=)
<u>4c</u>	Н	p-Br-C <sub>6</sub> H <sub>4</sub> -CH <sub>2</sub>	18	139-140	4.24 (s, SCH <sub>2</sub> ); 6.21 (s, -CH=); 7.22-7.63 (m, 9H arom); 7.67 (s, -CH=)
<u>4d</u>	CH3	сн3	11	109–111	1.88 (s, CH <sub>3</sub> ); 2.63 (s, SCH <sub>3</sub> ); 7.25-7.55 (m, 5H arom); 7.63 (s, -CH=)

Table 1. 2-Alkylthio-6-phenyl-4H-thiopyran-4-ones <u>3a-d</u> and 5-Alkylthio-2-benzylidene-3(2H)-thiophenones <u>4a-d</u>

a) <u>4b</u>: in acetone-d<sub>6</sub>

In the <sup>1</sup>H NMR spectra the olefinic proton of the benzylidene group in <u>4</u> ( $\int$  7.62-7.67 ppm) shows a significant downfield shift whereas the H<sub>5</sub>signal in <u>3</u> appears at  $\int$  6.8-7.1 ppm. In addition, the doubtless assignment of the ring size is possible via <sup>13</sup>C,<sup>1</sup>H-spin-spin-coupling owing to the very characteristic vicinal coupling between the carbonyl carbon atom and the exocyclic olefinic proton in the five-membered ring <u>4</u>.<sup>10</sup>

## References and Notes

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- 7. The following procedure was used: Sodium hydride (15 mmol) is added to a solution of acetylenic ketone <u>1</u> (15 mmol) in dry DMF (50 ml) at room temperature. After 2 h alkyl halide (15 mmol) is added and stirring is continued for 3 h. The mixture is poured into ice-water (400 ml). <u>3</u> and <u>4</u> are separated by using column chromatography (Al<sub>2</sub>O<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>) and recrystallized from petroleum ether.
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- 9. Satisfactory elemental analyses and exact mass molecular weights were obtained for all new compounds.
  - <u>3a</u>: <sup>13</sup>C NMR (CDCl<sub>3</sub>): √ 16.23; 124.78; 126.43; 126.72; 129.30; 130.75; 135.53; 152.65; 154.90; 180.36 ppm.
  - <u>4a</u>: <sup>13</sup>C MMR (CDCl<sub>3</sub>): **d** 16.36; 116.06; 129.10; 130.16; 130.50; 130.67; 132.19; 134.10; 172.05; 188.10 ppm.
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