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2-Substituted tetrahydro- and cyclopentathiophenes **2** were produced in high yields by treatment of the semi-cyclic trisubstituted 1,4-diketones **1** such as 2-phenacylcyclohexan-1-one, 2-acetyl-cyclohexan-1-one, and 2-phenacylcyclopentan-1-one, with Lawesson's reagent.

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2-Bis(*p*-methoxyphenyl)-1,3-dithiaphosphphetane-2,4-disulfide (Lawesson's reagent; LR) is known to be a most effective thionation reagent for a wide variety of carbonyl compounds [1]. It is reported that treatment of bifunctional substrates with LR undergoes ring closure to form heterocycles [2]. Recently, Shridhar *et al.* [3] reported that the interaction of tri- and tetra-substituted butane-1,4-diones with LR resulted in the formation of a mixture of the thiophenes and furans in varying proportion, while that of di-substituted butane-1,4-diones with LR produced the thiophenes exclusively. We now report that semi-cyclic 1,4-diketones **1**, which are regarded as tri-substituted butane-1,4-diones, reacted with LR to give the thiophene derivatives **2** exclusively in high yields.

A mixture of semi-cyclic 1,4-diketones **1a-e,g** and equimolar of Lawesson's reagent (LR) in a mixed benzene-dimethoxyethane solution was heated under reflux to give 2-substituted 4,5,6,7-tetrahydrothiophenes **2a-e** and cyclopentathiophene (**2g**) in 58-99% yields. The structure of the products **2** was elucidated on the basis of spectral data and elemental analyses. The yield of 2-phenyl-4,5,6,7-tetrahydrothiophene (**2a**) decreased to about 1/2 by use of 0.5 mole of LR per mole of 2-phenacyl-cyclohexan-1-one

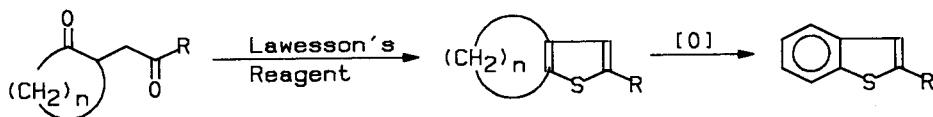
(**1a**). Consequently, the reaction presumably involves the formation of 1,4-dithioxo intermediate which undergoes cyclization and elimination of hydrogen sulfide to give **2**. 2-Phenyl- (**2a**) and 2-methyl-4,5,6,7-tetrahydrothiophene (**2e**) thus obtained were easily oxidized with chloranil or 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) to give the corresponding 2-substituted benzothiophenes **3a,e**. On the other hand, treatment of 4-oxo ester **1f** with LR gave an intractable mixture.

In conclusion, the reaction described here would be a facile method for the synthesis of 2-substituted 4,5,6,7-tetrahydrothiophenes **2** and benzothiophenes **3**.

EXPERIMENTAL

The Reaction of 1,4-Diketones **1a-g** with Lawesson's Reagent.

A solution of the 1,4-diketone (**1**, 1 mmole) and Lawesson's reagent (LR, 1.1 mmole) in benzene-dimethoxyethane (20-10 ml) was heated under reflux for 1 hour. After removal of the solvent *in vacuo*, the residual oil was chromatographed on a silica gel column (Wakogel C-300, flash chromatography) with benzene-hexane (1:4) as eluant to yield the corresponding tetrahydro-, **2a-e**, and cyclopentathiophenes **2g**.



n	R	Yield (%)	Yield (%)
1a	Ph	2a 91 (47) ^a	3a 91 (79) ^b
1b	<i>p</i> -MeC ₆ H ₄	2b 99	3e 41
1c	<i>p</i> -MeOC ₆ H ₄	2c 88	
1d	<i>p</i> -ClC ₆ H ₄	2d 78	
1e	Me	2e 67	
1f	OE _t	2f - ^c	
1g	Ph	2g 58	

^a0.5 eq. molar of LR was used. ^bDDQ was used as an oxidizing agent

^cIntractable mixture.

Table 1

The Yield and NMR Spectral Data of Tetrahydro- and Cyclopentathiophenes **2** and Benzothiophenes **3**

	Yield (%)	¹ H-NMR (Deuteriochloroform) (δ)	¹³ C-NMR (Deuteriochloroform) (δ)
2a	91 (47) [a]	1.60 (4H, m), 2.40-2.90 (4H, m), 6.95 (1H, s), 7.05-7.66 (5H, m)	22.9 (t), 23.6 (t), 25.1 (t), 25.6 (t), 123.7 (d), 125.4 (d), 126.9 (d), 128.7 (d), 134.8 (s), 135.5 (s), 136.3 (s), 140.3 (s)
2b	99	1.62-1.94 (4H, m), 2.32 (3H, s), 2.44-2.82 (4H, m), 6.90 (1H, s), 7.11 (2H, d, J = 7.8 Hz), 7.42 (2H, d, J = 7.8 Hz)	21.1 (q), 22.9 (t), 23.6 (t), 25.0 (t), 25.6 (t), 123.2 (d), 125.4 (d), 129.3 (d), 132.1 (s), 134.8 (s), 136.1 (s), 136.6 (s), 140.5 (s)
2c	88	1.65-1.95 (4H, m), 2.50-2.82 (4H, m), 3.78 (3H, s), 6.87 (1H, s), 6.85 (2H, d, J = 8.8 Hz), 7.45 (2H, d, J = 8.8 Hz)	22.9 (t), 23.7 (t), 25.0 (t), 25.6 (t), 55.3 (q), 114.1 (d), 122.7 (d), 126.7 (d), 127.8 (s), 134.4 (s), 136.2 (s), 140.2 (s), 158.8 (s)
2d	78	1.60-1.98 (4H, m), 2.38-2.84 (4H, m), 6.91 (1H, s), 7.21-7.58 (4H, m)	22.9 (t), 23.6 (t), 25.1 (t), 25.6 (t), 124.1 (d), 126.5 (d), 128.8 (d), 132.5 (s), 133.4 (s), 136.0 (s), 136.5 (s), 138.9 (s)
2e	67	1.61-1.95 (4H, m), 2.24-2.75 (4H, m), 2.40 (3H, s), 6.39 (1H, s)	15.5 (q), 23.1 (t), 23.8 (t), 24.9 (t), 25.6 (t), 125.8 (d), 133.2 (s), 135.0 (s), 135.8 (s)
2g	58	2.25-2.97 (6H, m), 7.02 (1H, s), 7.00-7.95 (5H, m)	28.4 (t), 29.0 (t), 29.3 (t), 118.4 (d), 125.3 (d), 126.9 (d), 128.7 (d), 135.5 (s), 141.8 (s), 147.2 (s)
3a	91 (79) [b]	7.16-7.92 (10H, m)	119.4 (d), 122.2 (d), 123.5 (d), 124.3 (d), 124.4 (d), 126.4 (d), 128.2 (d), 128.9 (d), 134.3 (s), 139.1 (s), 140.6 (s), 144.2 (s)
3e	41	2.53 (3H, d, J = 1.5 Hz), 6.93 (1H, br d, J = 1.5 Hz), 7.09-7.39 (2H, m), 7.53-7.78 (2H, m)	16.1 (q), 121.6 (d), 122.0 (d), 122.5 (d), 123.3 (d), 124.0 (d), 139.7 (s), 140.5 (s), 140.8 (s)

[a] 0.5 equimolar of LR was used. [b] DDQ was used as oxidizing agent.

2-Phenyl-4,5,6,7-tetrahydrothiophene (2a).

This compound had mp 79-80° (lit [4] 82.5-83.5°); ir (potassium bromide): 1590, 1500, 1440, 835, 760, 700 cm⁻¹.

2-p-Methylphenyl-4,5,6,7-tetrahydrothiophene (2b).

This compound had mp 63-64°; ir (potassium bromide): 1505, 1440, 1105, 815, 805 cm⁻¹.

Anal. Calcd. for C₁₅H₁₆S: C, 78.89; H, 7.06. Found: C, 79.15; H, 7.13.

2-p-Methoxyphenyl-4,5,6,7-tetrahydrothiophene (2c).

This compound had mp 117-118°; ir (potassium bromide): 1605, 1515, 1440, 1245, 1035, 825 cm⁻¹.

Anal. Calcd. for C₁₅H₁₆OS: C, 73.73; H, 6.60. Found: C, 74.06; H, 6.65.

2-p-Chlorophenyl-4,5,6,7-tetrahydrothiophene (2d).

This compound had mp 122-123°; ir (potassium bromide): 1495, 1435, 1085, 1000, 820, 810 cm⁻¹.

Anal. Calcd. for C₁₄H₁₃ClS: C, 67.59; H, 5.26. Found: C, 67.71; H, 5.29.

2-Methyl-4,5,6,7-tetrahydrothiophene (2e).

This compound had bp 85°/2 mm Hg (lit [5] 110-111°/19 mm Hg); ir (film): 1440, 1200, 1120, 830, 810 cm⁻¹.

2-Phenylcyclopentathiophene (2g).

This compound had mp 65-65.5°; ir (potassium bromide): 1590, 1490, 835, 750, 690 cm⁻¹.

Anal. Calcd. for C₁₃H₁₂S: C, 77.95; H, 6.03. Found: C, 78.01; H, 6.09.

Oxidation of 2-Substituted 4,5,6,7-Tetrahydrothiophenes 2a,e.

A mixture of the 4,5,6,7-tetrahydrothiophene **2** (200 mg) and Chloranil

(or DDQ) (2.5 equimolar) in toluene (30 ml) was refluxed under argon for 20 hours. An usual work-up as described above gave 2-substituted benzothiophene **3**.

2-Phenylbenzothiophene (3a).

This compound had mp 170-171° (lit [6] 170-172°); ir (potassium bromide) 1480, 1440, 820, 750, 720, 680 cm⁻¹.

2-Methylbenzothiophene (3e).

This compound had mp 50° (lit [7] 51-52°); ir (potassium bromide) 1455, 1430, 1200, 830, 745, 725 cm⁻¹.

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