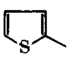
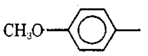
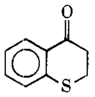
Table I. Synthesis of 4*H*-Thiopyran-4-ones[13]

	2[e]		3[f]		4[g]	
R	Mp (bp), °C	Yield,[a] %	Mp (bp), °C	Yield, %	Mp (bp), °C	Yield,[a] %
Ph	87–89[2]	100[3]	(115–130, 2.4 μ) 51–54	100[a] (93)[b]	120–125 (131–132)[c]	98
	85–89	95	89	47[b]	149.7	89
	168–169	77[4]	115.4	100[a]	158.6	88
H	59–61		(56–58, 0.9 mm)[15]	100[a] (92)[b]	105–107[16]	62[d]
	(154, 12 mm)		70–71[17]	100[a] (96)[b]		

[a] Yield of substantially pure product which is suitable for subsequent use. [b] Yield of analytically pure product. [c] Analytical sample obtained by recrystallization from EtOAc (lit.[3] mp 132–133 °C). [d] Some Se-containing by-products were also formed, but not characterized (cf. ref 10). [e] Registry no. are, respectively, 37014-01-0, 62461-51-2, 2573-84-4, 1072-72-6, 3528-17-4. [f] Registry no. are, respectively, 60839-95-4, 62461-52-3, 62461-53-4, 57242-69-0, 491-39-4. [g] Registry no. are, respectively, 1029-96-5, 62461-54-5, 62461-55-6, 1003-41-4.

over a 2-h period followed by a period of 2 h at room temperature. Methylene chloride was removed under vacuum at 30–35 °C and replaced with 400 mL of ether. The insoluble, precipitated succinimide was broken up manually, removed by filtration, and washed thoroughly with ether until colorless. The combined ethereal extract was dried ($MgSO_4$) and concentrated to give 51 g (~100%) of essentially pure (assay by TLC) product as a light brown, viscous oil. NMR [δ 3.05 [t, 2, $-C(=O)\mathbf{CH_2}CH(S)Ph$], 4.65 [dd, 1, $-CH_2\mathbf{CH}(S)Ph$], 6.5 (s, 1, $-\mathbf{CH}=CPh$), and 7.4 (m, 10, ArH)] showed the crude material to contain only traces of ether as a contaminant. An analytical sample was obtained by vacuum distillation of a portion (8 g) of this material at bp 115–130 °C (2–4 μ), from which 7.0 g (93%) of pure 2,6-diphenyl-4*H*-dihydrothiopyran-4-one was isolated (slowly crystallized on standing, mp 51–54 °C).

2,6-Bis(2-thienyl)tetrahydro-4*H*-thiopyran-4-one (2, R = 2-Thienyl). A mixture of 24 g (0.097 mol) of bis(2-thienal)acetone (prepared in quantitative yield by the procedure described for the preparation of dibenzalacetone),[14] 20 g of sodium acetate, and 200 mL of alcohol was refluxed while hydrogen sulfide was passed slowly into the solution for 5 h. The mixture was chilled, and the solid was collected and washed with water. The filtrate was diluted with 100 mL of water and extracted with methylene chloride. The extract was dried ($MgSO_4$) and the solvent removed. The solid residue was combined with the original solid to give 25 g (91%) of product: mp 85–89 °C; NMR δ 3.0 (m, 4, methylenes), 4.54 (m, 2, methines) and 6.7–7.2 (m, 6, thiophene).

2,6-Bis(2-thienyl)dihydro-4*H*-thiopyran-4-one (3, R = 2-Thienyl). To an ice-cooled and well-stirred solution of 15 g (0.0535 mol) of 2 (R = 2-thienyl) and 4.65 g (0.059 mol) of pyridine in 200 mL of methylene chloride was added 7.4 g (0.054 mol) of powdered NCS in ca. 10 min. The brown solution was allowed to slowly equilibrate to ambient temperature under nitrogen for 4 h and worked up by washing with 200 mL of water. Methylene chloride extracts were separated and concentrated in vacuo to give 14.7 g of a dark brown, gummy solid which was purified by column chromatography (silica gel, Wöelm dry column grade activity III, 1.75 × 19 in. column, wet packed with hexanes). Elution with benzene–hexanes (1:1 v/v) afforded first 2.4 g of unreacted starting material followed by a total of 5.95 g (47% based on consumed 2) of the desired crystalline product: NMR δ 2.95 (d, J = 8 Hz, 2, methylene), 4.74 (t, J = 8 Hz, 1, methine), 6.27 (s, 1, olefinic), and 6.45–7.5 (m, 6, thiophene); mass spectrum *m/e* 278 (M^+). An analytical sample was obtained by recrystallization, mp 89 °C (hexanes).

2,6-Bis(2-thienyl)-4*H*-thiopyran-4-one (4, R = 2-thienyl). A mixture of 3.4 g (0.0122 mol) of 3 (R = 2-thienyl) and 1.9 g (0.017 mol) of selenium dioxide in 100 mL of toluene was subjected to azeotropic distillation for 25 h (or until TLC assay showed the disappearance of starting material). The toluene solution, after being freed from deposited selenium metal, was concentrated in vacuo giving 3.05 g (89%) of an essentially pure crop of brown, crystalline product: NMR δ 6.8 (m, 4) and 7.1 (m, 4); mass spectrum *m/e* 276 (M^+), 248 ($M^+ - CO$). An analytical sample was obtained by recrystallization from benzene and hexanes in the form of dark purple needles, mp 149.7 °C.

Registry No.—1 (R = 2-thienyl), 62461-56-7; 1 (R = Ph), 538-58-9; 1 (R = MeO-*p*-C_6H_4), 2051-07-2; 1 (R = H), 1890-28-4; acrylophenone, 768-03-6.

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Reductive Coupling of 1,3-Dithiolium with Zinc

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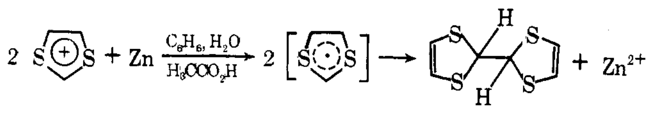
This note describes the synthesis of 2,2′-bi(dithiolyl) (1), in excellent yield, by a zinc reductive coupling reaction. A probable route for formation of the desired compound is shown in Scheme I.

Scheme I



1

The first reported procedure for the synthesis of $(C_3H_3S_2)_2$ from 1,3-dithiole-2-thione is that of Challenger et al.[1] However, no overall yield was given. The use of zinc for reductive couplings of six-membered heterocyclic cations has been reported previously[2–4] to give rise to dimers coupled in the γ,γ' positions. More recently, however, Siedle and Johannesen[5] reported the synthesis of 2,2′-bi(1,3-dithiolyl), in moderate yield, via the exotic reducing agent sodium bis(diglyme)hexacarbonyl vanadate. The advantages of our method are (1) it involves the use of an inexpensive, common reducing agent; and (2) the yield is much higher.

Experimental Section[6]

In a 250-mL Morton flask fitted with a magnetic stirrer were placed 50 mL of benzene, 50 mL of distilled water, 50 mL of glacial acetic acid, 1.725 g (6.96×10^{-3} mol) of 1,3-dithiolium hexafluorophosphate,[7] and 0.920 g (1.41×10^{-2} g-atom) of zinc dust. After the reaction mixture was stirred vigorously for ca. 12 h, the layers were separated, and the aqueous layer was extracted once with 50 mL of benzene. The organic layers were combined, washed with 150 mL of dilute potassium chloride (three times, 50 mL each), dried (potassium carbonate), filtered, and concentrated to dryness on the rotary evaporator. The semicrystalline residue was crystallized from cold acetone to give 0.660 g (92%) of 2,2′-bi(dithiolyl) as white needles (mp 150.9–151.6 °C; lit.[5] mp 150–151 °C). The IR and ^1H NMR spectra of this compound were in substantial agreement with those reported by Siedle and Johannesen.

Registry No.—**1**, 23625-38-9; 1,3-ditholium hexaflurophosphate, 55298-73-2; zinc, 7440-66-6.

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Oxygen Transfer Reaction in Acetonylation of 2-Methylcyclohexane-1,3-dione with 2-Nitropropene

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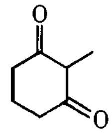
In the previous paper, we (T.Y., M.K., and A.Y.) reported that the KF-catalyzed reaction of 2-methylcyclohexane-1,3-dione (**1**) and 2-nitropropene in hot xylene resulted in the formation of 2-methyl-2-acetonylcyclohexane-1,3-dione (**3a**) in good yield.[3] Obviously, the Michael addition of **1** and 2-nitropropene occurred first to yield nitrodione **2a**, which was then converted into **3a** under the prolonged reaction conditions, as demonstrated by the fact that **2a** was isolated from the reaction mixture at the initial stage and then converted into **3a** under similar conditions. 2-Nitrooctane and 2-methyl-2-(β-nitroethyl)cyclohexane-1,3-dione[3] (**2b**), however, were unchanged on similar treatment. The fact that 2-nitrooctane, a typical secondary nitroalkane, is inert under the above reaction conditions indicates that the nitro group in **2a** would be activated by the keto group on the cyclohexane ring to be converted into a keto group. Unsuccessful conversion of **2b** into the corresponding keto aldehyde **3b** demonstrates that a nitro ketone intermediate is required to have a secondary nitro group.[4]



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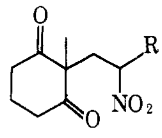
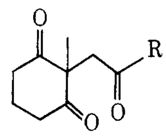
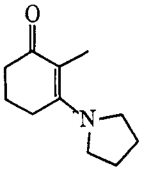


2a, R = Me
b, R = H



3a, R = Me
b, R = H



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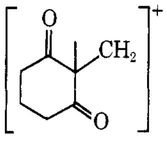

9

$[CH_3C\equiv O]^+$

10

Initially we assumed an equilibration between an aci form (**4**) of **2a** and structure **5** which would probably be responsible to such activation of the nitro group by the keto group (Scheme I). If this is the case, the attack by a nucleophile such as hydroxide anion, a probable nucleophilic species in this case, could occur in two ways, i.e., in **6**, on the carbon adjacent to the nitrogen atom and on the carbonium carbon on the cyclohexane ring. Our provisional transformation into the final product after this stage is shown in Scheme I. Provided that the transformation is limited to the pathway in which the carbonium carbon in **6** is attacked by hydroxide anion, an oxygen transfer from the keto group in **4** to the side chain in the product may occur as shown by asterisked O in the scheme, while no one can anticipate such oxygen transfer in the alternative pathway.

To test on the basis of the above presumption whether or not the ketonic oxygen atoms on the cyclohexane ring could indeed migrate, we decided to use 2-methylcyclohexane-1,3-dione labeled with ^{18}O as the starting material in the acetonylation and to examine the resultant product by mass spectrometric analysis.

Acid hydrolysis of 2-methyl-3-(1-pyrrolidinyl)cyclohex-2-en-1-one (**8**)[5] in water enriched with $H_2{}^{18}O$ gave the requisite 2-methylcyclohexane-1,3-dione with one of its ketonic oxygen atoms labeled with the isotopic oxygen. No double labeling of **1** took place during the hydrolytic treatment since no molecular ion peak corresponding to $C_7H_{10}{}^{18}O_2$ was detectable in the mass spectrum of the labeled **1**.

The molecular ion peak enhancement at *m/e* 128 relative to that at *m/e* 126 showed a 28.9% incorporation of ^{18}O into **1**.[6] The labeled dione **1** was made to react with 2-nitropropene under standard conditions (Experimental Section) affording the labeled trione **3a** with little loss in ^{18}O content (26.9%). No doubly labeled species was detectable in the mass spectrum of the labeled **3a**.