Synthesis of 3,4-Dihydro-2*H*-thiopyrans by the Reaction of 4,5-Dihydrothiophenium-1-bis[ethoxy(and methoxy)carbonyl]methylides with Sodium Iodide

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Sulfonium ylides **1a-h** reacted with sodium iodide to afford the corresponding thiopyrans **2a-h**. On the other hand, compounds **1a-d** were treated with thionyl chloride to give the ring opening products **3a-d**. The reaction of compounds **3a-d** with sodium iodide and triethylamine provided the corresponding thiopyrans **2a-d**.

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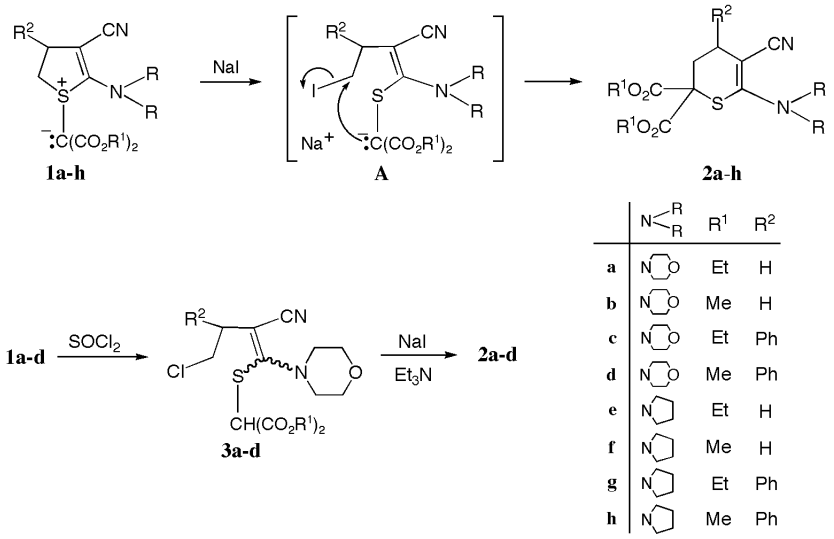
Thiopyrans are attractive compounds for chemical synthesis because their similarity with pyrans hints at useful biological properties that should be relatively easy to discover due to their simple framework [1,2]. Rearrangement of sulfonium ylides is known to produce thiopyrans [3,4]. This paper presents a new synthesis of thiopyrans from sulfonium ylides. In the course of our studies on heterocyclic enaminonitriles, we have shown that the reactions of 2-amino-4,5-dihydro-3-furancarbonitriles with sodium iodide [5,6] or titanium(IV) chloride [7] proceed through an initial ring opening between the oxygen and the 5-position of the furan ring by the attack of a halide ion on the 5-position of the furan ring. Under the same conditions, in the case of the corresponding 4,5-dihydro-3-thiophene carbonitriles, ring opening reactions did not take place. In contrast with 4,5-dihydro-3-thiophenecarbonitriles, the sulfonium ylides **1** of 4,5-dihydro-3-thiophenecarbonitriles undergo cleavage at the sulfur—C-5 bond and subsequent recyclization in the presence of a base [8]. These findings suggest that the sulfur—C-5 bond of the sulfonium ylides is more easily cleaved than that of 4,5-dihydro-3-thiophenecarbonitriles. Hence, we examined the reaction of the sulfonium ylides with sodium iodide to see whether or not cleavage at the sulfur—C-5 bond takes place. The starting compounds dihydrothiophenium-1-bis(ethoxycarbonyl)methylides **1a**,**c**,**e**,**g** were prepared by previously reported method [8]. Dihydrothiophenium-1-bis(methoxycarbonyl)-methylides **1b**,**d**,**f**,**h** were synthesized by the reaction of the corresponding 2-amino-4,5-dihydro-3-thiophenecarbonitriles [8] with dimethyl diazomalonate [9] in the presence of rhodium(II) acetate dimer.

When a mixture of sulfonium ylides **1a,c-h** and sodium iodide (2 equivalents) in acetone was refluxed for 7 hours, the corresponding 3,4-dihydro-2*H*-thiopyrans **2a,c-h** were obtained, and the expected ring opening products could not be isolated. In a similar manner, no reaction occurred in the case of **1b**, and **1b** was recovered unchanged. When *N*,*N*-dimethylformamide was used in place of acetone, compound **1b** reacted with sodium iodide at 100° to provide **2b**. Although ring expansion of thiophenes to thiopyrans *via* a process involving sulfonium ylide intermediates has been reported [3,4], to our knowledge, ring expansion of sulfonium ylides by use of sodium iodide has not been

Scheme



	N(R)R	R^1	R^2
a	morpholino	Et	H
b	morpholino	Me	H
c	morpholino	Et	Ph
d	morpholino	Me	Ph
e	pyrrolidino	Et	H
f	pyrrolidino	Me	H
g	pyrrolidino	Et	Ph
h	pyrrolidino	Me	Ph

reported. A reasonable pathway for the formation of **2** is shown in Scheme. An iodide ion attacks at the 5-position of **1** to form the intermediate carbanion **A**, which then undergoes fast intramolecular cyclization to give **2**.

Subsequently, the reaction of **1a-d** with thionyl chloride resulted in the formation of the expected ring opening products **3a-d** in moderate yields. Finally, we synthesized **2a-d** from **3a-d**. Compounds **3a-d** were allowed to react with sodium iodide and triethylamine in refluxing acetone to afford the desired **2a-d** together with the corresponding 2-amino-4,5-dihydro-3-thiophenecarbonitriles. The structural assignments of **2** and **3** were made on the basis of elemental analyses and the spectral data.

EXPERIMENTAL

All melting points are uncorrected. The ir spectra were recorded on a JASCO A-302 spectrometer. The ^{1}H nmr spectra were measured in deuteriochloroform on a HITACHI R-90 H spectrometer (90 MHz). Chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane as internal standard. Elemental analyses were performed on a HERAUS CHNO-RAPID analyzer.

General Procedure for the Preparation of 4,5-Dihydrothiophenium-1-bis(methoxycarbonyl)methylides **1b**,**d**,**f**,**h**.

A mixture of 4,5-dihydro-2-morpholino(or -2-pyrrolidino)-3-thiophenecarbonitriles [8] (20 mmoles), dimethyl diazomalonate [9] (4.74 g, 30 mmoles) and rhodium(II) acetate dimer (80 mg, 0.18 mmole) in toluene (40 ml) was refluxed for 2 hours. After removal of the solvent *in vacuo*, the residue was purified by column chromatography on alumina with methylene chloride-acetone (4:1) as the eluent to give **1b**,**d**,**f**,**h**.

3-Cyano-4,5-dihydro-2-morpholinothiophenium-1-bis(methoxycarbonyl)methylide (**1b**).

This compound was obtained as colorless prisms (2.94 g, 45%), mp 110-112° (methylene chloride-petroleum ether); ir (potassium bromide): ν 2210 (C≡N), 1630 (C=O) cm^{-1}; ^{1}H nmr: δ 3.42-3.73 [m, 12H, 4-H, 5-H, 4xCH_2 (morpholine)], 3.73 ppm (s, 6H, 2xCO_2CH_3).

Anal. Calcd. for $C_{14}H_{18}N_2O_5S$: C, 51.52; H, 5.56; N, 8.58. Found: C, 51.46; H, 5.51; N, 8.61.

3-Cyano-4,5-dihydro-2-morpholino-4-phenylthiophenium-1-bis(methoxycarbonyl)methylide (**1d**).

This compound was obtained as colorless needles (5.09 g, 63%), mp 133-135° (acetone-petroleum ether); ir (potassium bromide): ν 2195 (C≡N), 1620 (C=O) cm^{-1}; ^{1}H nmr: δ 3.28-4.19 [m, 11H, 4-H, 5-H, 4xCH_2 (morpholine)], 3.76 (s, 6H, 2xCO_2CH_3), 7.35-7.50 ppm (m, 5H, aromatic H).

Anal. Calcd. for $C_{20}H_{22}N_2O_5S$: C, 59.69; H, 5.51; N, 6.96. Found: C, 59.41; H, 5.49; N, 7.04.

3-Cyano-4,5-dihydro-2-pyrrolidinothiophenium-1-bis(methoxycarbonyl)methylide (**1f**).

This compound was obtained as colorless prisms (2.79 g, 45%), mp 132-133° (methylene chloride-petroleum ether); ir (potassium bromide): ν 2198 (C≡N), 1630 (C=O) cm^{-1}; ^{1}H nmr: δ 1.80-2.03 [m, 4H, 2xCH_2 (pyrrolidine)], 3.44-3.72 [m, 8H, 4-H, 5-H, 2xCH_2 (pyrrolidine)], 3.76 ppm (s, 6H, 2xCO_2CH_3).

Anal. Calcd. for $C_{14}H_{18}N_2O_4S$: C, 54.18; H, 5.85; N, 9.03. Found: C, 54.12; H, 5.77; N, 9.06.

3-Cyano-4,5-dihydro-4-phenyl-2-pyrrolidinothiophenium-1-bis(methoxycarbonyl)methylide (**1h**).

This compound was obtained as colorless needles (4.49 g, 58%), mp 194-196° (chloroform-petroleum ether); ir (potassium bromide): ν 2180 (C≡N), 1625 (C=O) cm^{-1}; ^{1}H nmr: δ 1.76-2.06 [m, 4H, 2xCH_2 (pyrrolidine)], 3.46-4.15 [m, 7H, 4-H, 5-H, 2xCH_2 (pyrrolidine)], 3.76 (s, 6H, 2xCO_2CH_3), 7.30-7.52 ppm (m, 5H, aromatic H).

Anal. Calcd. for $C_{20}H_{22}N_2O_4S$: C, 62.16; H, 5.74; N, 7.25. Found: C, 61.89; H, 5.71; N, 7.24.

General Procedure for the Preparation of **2a-h** from **1a-h**.

Procedure A.

A mixture of **1a**,**c-h** (10 mmoles) and NaI (3.00 g, 20 mmoles) in acetone (20 ml) was refluxed for 7 hours. After removal of the solvent *in vacuo*, cold water was added to the residue. The resulting mixture was extracted with chloroform. The extract was dried over anhydrous sodium sulfate and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel with chloroform as the eluent to give **2a**,**c-h**. Further the elution with chloroform-acetone (4:1) gave the starting material **1e** (0.89 g, 26%), **1f** (0.63 g, 20%) and **1h** (0.43 g, 11%), respectively.

Procedure B.

A mixture of **1b** (3.26 g, 10 mmoles) and NaI (1.50 g, 10 mmoles) in *N*,*N*-dimethylformamide (20 ml) was heated at 100° with stirring for 5 hours. After work-up as described for the preparation of **2a,c-h** from **1a,c-h**. The residue was purified by column chromatography on silica gel with chloroform as the eluent to give **2b**.

Diethyl 5-Cyano-3,4-dihydro-6-morpholino-2*H*-thiopyran-2,2-dicarboxylate (**2a**).

This compound was obtained as pale yellow oil (3.15 g, 89%); ir (neat): ν 2190 (C≡N), 1740 (C=O) cm^{-1}; ^{1}H nmr: δ 1.28 (t, J = 7 Hz, 6H, 2x$CO_2CH_2CH_3$), 2.46 (s, 4H, 3-H, 4-H), 3.29-3.40 [m, 4H, 2xCH_2 (morpholine)], 3.63-3.79 [m, 4H, 2xCH_2 (morpholine)], 4.26 ppm (q, J = 7 Hz, 4H, 2x$CO_2CH_2CH_3$).

Anal. Calcd. for $C_{16}H_{22}N_2O_5S$: C, 54.22; H, 6.26; N, 7.90. Found: C, 53.98; H, 6.17; N, 8.12.

Dimethyl 5-Cyano-3,4-dihydro-6-morpholino-2*H*-thiopyran-2,2-dicarboxylate (**2b**).

This compound was obtained as colorless prisms (2.93 g, 90%), mp 50-52° (diethyl ether-petroleum ether); ir (potassium bromide): ν 2190 (C≡N), 1740 (C=O) cm^{-1}; ^{1}H nmr: δ 2.46 (s, 4H, 3-H, 4-H), 3.30-3.40 [m, 4H, 2xCH_2 (morpholine)], 3.69-3.81 [m, 4H, 2xCH_2 (morpholine)], 3.81 ppm (s, 6H, 2xCO_2CH_3).

Anal. Calcd. for $C_{14}H_{18}N_2O_5S$: C, 51.52; H, 5.56; N, 8.58. Found: C, 51.78; H, 5.76; N, 8.82.

Diethyl 5-Cyano-3,4-dihydro-6-morpholino-4-phenyl-2*H*-thiopyran-2,2-dicarboxylate (**2c**).

This compound was obtained as pale yellow oil (4.14 g, 96%); ir (neat): ν 2200 (C≡N), 1740, 1730 (C=O) cm^{-1}; ^{1}H nmr: δ 1.05 (t,

J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.24 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 2.77 (dd, J = 5.5, 16 Hz, 1H, 3-H), 3.13 (dd, J = 7, 16 Hz, 1H, 3-H), 3.31-3.57 [m, 4H, 2xCH_2 (morpholine)], 3.67-3.81 [m, 4H, 2xCH_2 (morpholine)], 3.92 (dd, J = 5.5, 7 Hz, 1H, 4-H), 4.23 (q, J = 7 Hz, 4H, 2x$CO_2CH_2CH_3$), 7.27 ppm (s, 5H, aromatic H).

Anal. Calcd. for $C_{22}H_{26}N_2O_5S$: C, 61.38; H, 6.09; N, 6.51. Found: C, 61.11; H, 5.97; N, 6.56.

Dimethyl 5-Cyano-3,4-dihydro-6-morpholino-4-phenyl-2*H*-thiopyran-2,2-dicarboxylate (**2d**).

This compound was obtained as colorless prisms (3.82 g, 95%), mp 68-70° (diethyl ether-petroleum ether); ir (potassium bromide): ν 2180 (C≡N), 1735 (C=O) cm^{-1}; ^1H nmr: δ 2.75 (dd, J = 5.5, 16 Hz, 1H, 3-H), 3.15 (dd, J = 7, 16 Hz, 1H, 3-H), 3.20-3.78 [m, 8H, 4xCH_2 (morpholine)], 3.45 (s, 3H, CO_2CH_3), 3.78 (s, 3H, CO_2CH_3), 4.20 (dd, J = 5.5, 7 Hz, 1H, 4-H), 7.27 ppm (s, 5H, aromatic H).

Anal. Calcd. for $C_{20}H_{22}N_2O_5S$: C, 59.69; H, 5.51; N, 6.96. Found: C, 59.96; H, 5.64; N, 7.15.

Diethyl 5-Cyano-3,4-dihydro-6-pyrrolidino-2*H*-thiopyran-2,2-dicarboxylate (**2e**).

This compound was obtained as colorless prisms (1.69 g, 50%), mp 37-38° (diethyl ether-petroleum ether); ir (potassium bromide): ν 2170 (C≡N), 1735 (C=O) cm^{-1}; ^1H nmr: δ 1.28 (t, J = 7 Hz, 6H, 2x$CO_2CH_2CH_3$), 1.83-1.98 [m, 4H, 2xCH_2 (pyrrolidine)], 2.43 (s, 4H, 3-H, 4-H), 3.56-3.71 [m, 4H, 2xCH_2 (pyrrolidine)], 4.26 ppm (q, J = 7 Hz, 4H, 2x$CO_2CH_2CH_3$).

Anal. Calcd. for $C_{16}H_{22}N_2O_4S$: C, 56.79; H, 6.55; N, 8.28. Found: C, 57.00; H, 6.61; N, 8.37.

Dimethyl 5-Cyano-3,4-dihydro-6-pyrrolidino-2*H*-thiopyran-2,2-dicarboxylate (**2f**).

This compound was obtained as colorless needles (1.74 g, 56%), mp 126-128° (acetone-petroleum ether); ir (potassium bromide): ν 2170 (C≡N), 1742 (C=O) cm^{-1}; ^1H nmr: δ 1.84-1.98 [m, 4H, 2xCH_2 (pyrrolidine)], 2.43 (s, 4H, 3-H, 4-H), 3.57-3.72 [m, 4H, 2xCH_2 (pyrrolidine)], 3.81 ppm (s, 6H, 2xCO_2CH_3).

Anal. Calcd. for $C_{14}H_{18}N_2O_4S$: C, 54.18; H, 5.85; N, 9.03. Found: C, 54.24; H, 5.93; N, 8.97.

Diethyl 5-Cyano-3,4-dihydro-4-phenyl-6-pyrrolidino-2*H*-thiopyran-2,2-dicarboxylate (**2g**).

This compound was obtained as colorless prisms (3.85 g, 93%), mp 92-93° (diethyl ether-petroleum ether); ir (potassium bromide): ν 2190 (C≡N), 1735 (C=O) cm^{-1}; ^1H nmr: δ 0.93 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.24 (t, J = 7 Hz, 3H, $CO_2CH_2CH_3$), 1.86-2.04 [m, 4H, 2xCH_2 (pyrrolidine)], 2.72 (dd, J = 7, 16 Hz, 1H, 3-H), 3.03 (dd, J = 7, 16 Hz, 1H, 3-H), 3.56-4.03 [m, 4H, 2xCH_2 (pyrrolidine)], 4.23 (t, J = 7 Hz, 1H, 4-H), 4.24 (q, J = 7 Hz, 4H, 2x$CO_2CH_2CH_3$), 7.27 ppm (s, 5H, aromatic H).

Anal. Calcd. for $C_{22}H_{26}N_2O_4S$: C, 63.75; H, 6.32; N, 6.76. Found: C, 63.50; H, 6.30; N, 6.73.

Dimethyl 5-Cyano-3,4-dihydro-4-phenyl-6-pyrrolidino-2*H*-thiopyran-2,2-dicarboxylate (**2h**).

This compound was obtained as colorless prisms (2.46 g, 64%), mp 125-127° (acetone-petroleum ether); ir (potassium bromide): ν 2180 (C≡N), 1740 (C=O) cm^{-1}; ^1H nmr: δ 1.85-2.10 [m, 4H, 2xCH_2 (pyrrolidine)], 2.76 (dd, J = 7, 16 Hz, 1H, 3-H), 3.06 (dd, J = 7, 16 Hz, 1H, 3-H), 3.40 (s, 3H, CO_2CH_3), 3.61-3.86 [m, 4H, 2xCH_2 (pyrrolidine)], 3.79 (s, 3H, CO_2CH_3), 4.21 (t, J = 7 Hz, 1H, 4-H), 7.28 ppm (s, 5H, aromatic H).

Anal. Calcd. for $C_{20}H_{22}N_2O_4S$: C, 62.16; H, 5.74; N, 7.25. Found: C, 62.03; H, 5.75; N, 7.24.

General Procedure for the Preparation of **3a-d** from **1a-d**.

A solution of **1a-d** (10 mmoles) and thionyl chloride (1.79 g, 15 mmoles) in chloroform (10 ml) was refluxed for 5 hours. After removal of the solvent *in vacuo*, the residue was basified with a saturated aqueous sodium hydrogen carbonate, and extracted with chloroform. The extract was dried over anhydrous sodium sulfate and concentrated *in vacuo*. The residue was purified by column chromatography on alumina with chloroform as the eluent to give **3a-d.**

Diethyl [(4-Chloro-2-cyano-1-morpholino-1-buten-1-yl)thio]propanedioate (**3a**).

This compound was obtained as pale yellow oil (2.17 g, 56%); ir (neat): ν 2200 (C≡N), 1735 (C=O) cm^{-1}; ^1H nmr: δ 1.30 (t, J = 7 Hz, 6H, 2x$CO_2CH_2CH_3$), 2.54-2.73 (m, 2H, 3-H), 2.85-3.01 (m, 2H, 4-H), 3.24-3.36 [m, 4H, 2xCH_2 (morpholine)], 3.70-3.80 [m, 4H, 2xCH_2 (morpholine)], 4.18 [s, 1H, C*H*$(CO_2CH_2CH_3)_2$], 4.26 ppm (q, J = 7 Hz, 4H, 2x$CO_2CH_2CH_3$).

Anal. Calcd. for $C_{16}H_{23}ClN_2O_5S$: C, 49.16; H, 5.93; N, 7.17. Found: C, 49.19; H, 5.67; N, 7.39.

Dimethyl [(4-Chloro-2-cyano-1-morpholino-1-buten-1-yl)thio]-propanedioate (**3b**).

This compound was obtained as pale yellow oil (2.61 g, 72%); ir (neat): ν 2200 (C≡N), 1735 (C=O) cm^{-1}; ^1H nmr: δ 2.55-2.71 (m, 2H, 3-H), 2.85-3.02 (m, 2H, 4-H), 3.25-3.37 [m, 4H, 2xCH_2 (morpholine)], 3.72-3.89 [m, 4H, 2xCH_2 (morpholine)], 3.80 (s, 6H, 2xCO_2CH_3), 4.23 ppm [s, 1H, C*H*$(CO_2CH_3)_2$].

Anal. Calcd. for $C_{14}H_{19}ClN_2O_5S$: C, 46.35; H, 5.28; N, 7.72. Found: C, 46.29; H, 5.23; N, 7.97.

Diethyl [(4-Chloro-2-cyano-1-morpholino-3-phenyl-1-buten-1-yl)thio]propanedioate (**3c**).

This compound was obtained as pale yellow oil (3.72 g, 80%); ir (neat): ν 2190 (C≡N), 1730 (C=O) cm^{-1}; ^1H nmr: δ 1.29 (t, J = 7 Hz, 6H, 2x$CO_2CH_2CH_3$), 2.82 (dd, J = 5.5, 11 Hz, 1H, 4-H), 3.19-3.35 [m, 5H, 4-H, 2xCH_2 (morpholine)], 3.69-3.83 [m, 4H, 2xCH_2 (morpholine)], 4.04-4.37 (m, 1H, 3-H), 4.19 [s, 1H, C*H*$(CO_2CH_2CH_3)_2$], 4.25 (q, J = 7 Hz, 4H, 2x$CO_2CH_2CH_3$), 7.32 ppm (s, 5H, aromatic H).

Anal. Calcd. for $C_{22}H_{27}ClN_2O_5S$: C, 56.59; H, 5.83; N, 6.00. Found: C, 56.78; H, 5.80; N, 6.25.

Dimethyl [(4-Chloro-2-cyano-1-morpholino-3-phenyl-1-buten-1-yl)thio]propanedioate (**3d**).

This compound was obtained as pale yellow oil (3.33 g, 76%); ir (neat): ν 2200 (C≡N), 1740 (C=O) cm^{-1}; ^1H nmr: δ 2.80-2.91 (m, 1H, 4-H), 3.21-3.39 [m, 5H, 4-H, 2xCH_2 (morpholine)], 3.70-3.82 [m, 4H, 2xCH_2 (morpholine)], 3.80 (s, 6H, 2xCO_2CH_3), 4.00-4.22 (m, 1H, 3-H), 4.22 [s, 1H, C*H*$(CO_2CH_3)_2$], 7.32 ppm (s, 5H, aromatic H).

Anal. Calcd. for $C_{20}H_{23}ClN_2O_5S$: C, 54.73; H, 5.28; N, 6.38. Found: C, 54.60; H, 5.56; N, 6.29.

General Procedure for the Preparation of **2a-d** from **3a-d**.

A mixture of **3a-d** (10 mmoles), NaI (3.00 g, 20 mmoles) and triethylamine (2.02 g, 20 mmoles) in acetone (20 ml) was

refluxed for 7 hours. After removal of the solvent *in vacuo*, cold water was added to the residue. The resulting mixture was extracted with chloroform. The extract was dried over anhydrous sodium sulfate and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel with chloroform as the eluent. The first fraction provided 4,5-dihydro-2-morpholino-3-thiophenecarbonitrile [8] [from **3a** (0.82 g): yield 42%, from **3b** (0.67 g): yield 34%] and 4,5-dihydro-2-morpholino-4-phenyl-3-thiophenecarbonitrile [8] [from **3c** (1.08 g): yield 40%, from **3d** (0.95 g): yield 35%]. The second fraction gave the corresponding thiopyrans **2a** (1.66 g, 47%), **2b** (1.71 g, 52%), **2c** (2.32 g, 54%) and **2d** (1.89 g, 47%), respectively. Compounds **2a-d** were identical with samples prepared from **1a-d** and sodium iodide on the basis of a comparison of the ir spectra.

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