final purification by sublimation gave 2.7 g (28%) of a yellow solid, mp 130–140° (lit.[3] mp 146–147°). This material was suitable for further transformations.

Benzyl (2-Methylthio-5-nitro)phenyl Ether (6b). A. By Condensation of 6a with 2.—The sodium salt of **6a** was prepared from 185 mg (1 mmol) of **6a** and 2 ml of a 0.5 *M* methanolic sodium methoxide solution. Methanol was evaporated and bromide **2a** (272 mg, 1 mmol) dissolved in 3 ml of DMF was added. The mixture was heated at 75° for 15 hr, poured into ice water, and extracted with methylene chloride. The organic phase was washed consecutively with 1 *N* NaOH, water, and saturated NaCl solution. Methylene chloride was evaporated and the residue was chromatographed on a silica gel column with benzene as the eluent. A yellow solid weighing 137 mg (50%) was obtained: mp 101–103°; ir (CCl_4) 1520, 1338 (NO_2), 1243, 1065 cm^{-1} (C═COC); nmr (CCl_4) δ 2.4 (s, 3 H, SCH_3), 5.1 (s, 2 H, OCH_2Ar), 7.35 (m, 8, Ar H).

Anal. Calcd for $C_{14}H_{13}NO_3S$: C, 61.08; H, 4.76; N, 5.09. Found: C, 60.84; H, 4.85; N, 5.31.

B. By Condensation of 6a with 7a.—Methylthio ether **6a** (185 mg, 1 mmol) was dissolved in 2 ml of a 0.5 *M* methanolic sodium methoxide solution and mixed with pyrrolidine **7a**[18] (254 mg, 1 mmol) in 1 ml of methanol. The mixture was refluxed for 8 hr and then allowed to stand overnight at room temperature. Methanol was evaporated, and the residue was extracted between 1 *N* NaOH and ether. The organic solution was dried and ether was removed. Chromatography of the residue as above gave a yellow solid. Its nmr and ir were identical with those of the sample obtained *via* method A.

C. By Condensation of 6a with 8.—A mixture of **8**[20] (132 mg, 0.5 mmol), 114 mg (0.55 mmol) of DCC, and 93 mg (0.5 mmol) of **6a** was heated in a flask purged with Ar at 110°. After 24 hr, the contents were washed with acetone and filtered. The filtrate was concentrated and the residue was extracted between CCl_4 and 1 *N* KOH. The organic phase was dried with saturated NaCl solution and then anhydrous $MgSO_4$. The residue left from evaporation of CCl_4 was triturated with petroleum ether (bp 30–60°). A yellow solid weighing 86 mg (62%) was obtained when the petroleum ether was removed. The solid had the same ir and nmr spectrum as the sample obtained *via* method A.

D. By Condensation of 6a with Benzyl Alcohol.—A mixture of benzyl alcohol (130 mg, 1.2 mmol), methylthio ether **6a** (185 mg, 1 mmol), and DCC (227 mg, 1.1 mmol) was heated at 105° for 81 hr under Ar. The contents were washed with CCl_4 and filtered. The filtrate was washed with 1 *N* KOH. The organic layer was dried and concentrated. A residue weighing 250 mg (91%) was obtained. Its spectral properties were identical with those of the sample obtained by method A.

***n*-Butyl (2-Methylthio-5-nitro)phenyl Ether (6d).**—A solution containing methylthiophenol **6a** (185 mg, 1 mmol) and 2 ml of 0.5 *M* methanolic NaOMe was evaporated to dryness. Then 3 ml of DMF was added, followed by 0.2 ml (177 mg, 1.9 mmol) of *n*-butyl chloride and a pinch of powdered potassium iodide. The mixture was heated at 62° for 12 hr, and then poured into a 1 *N* NaOH solution. The precipitate was filtered and sucked dry. The crude residue (**6d**) weighed 110 mg (45% yield), and gave only one major spot on tlc. Treatment of this material with methyl iodide and $AgClO_4$ gave the dimethylsulfonium salt, mp 123–127°.

Anal. Calcd for $C_{12}H_{18}NClO_7S$: C, 40.6; H, 5.07; N, 3.95. Found: C, 40.36; H, 5.11; N, 3.96.

***N*-Cbz-β-piperidinomethyl (2-Methylthio-5-nitro)phenyl Ether (12).**—A mixture of β-(hydroxymethyl)-*N*-Cbz-piperidine (**11**)[21] (125 mg, 0.50 mmol), DCC (114 mg, 0.55 mmol), and **6a** (93 mg, 0.5 mmol) was heated at 110° in a flask purged with Ar. After 24 hr, the contents were washed with acetone and filtered. The filtrate was worked up as desdribed for **6b** (method C). The residue was chromatographed on a preparative tlc plate (silica gel with fluorescent indicator, benzene–ethyl acetate, 20:1, as eluent). Two yellow bands were extruded. One had the same R_f and nmr spectrum as **6b**. The other slower migrating band, obtained as a thick oil, weighed 107 mg (51.5%): ir ($CHCl_3$) 1685 (C═O), 1510, 1334 (NO_2), 1240, 1065 cm^{-1} (C═COC); nmr ($CDCl_3$) δ 1.7 (m, 4 H, ring H), 2.42 (s, 3 H, SCH_3), 3.0 (m, 3 H, ring H), 3.98 (d, J = 5 Hz, 2 H, OCH_2–), 4.3 (m, 2 H, CHNCH), 5.14 (s, 2 H, CH_2Ar), 2.5 (m, 8 H, ArH).

This *N*-Cbz ether (**12**) was methylated with CH_3I and $AgClO_4$ in CH_2Cl_2 and the resulting sulfonium compound was treated with 70% $HClO_4$ to cleave the Cbz group. The diperchlorate ammoniosulfonium salt (**1**, X = O, m = 1, n = 3) was recrystallized from absolute ethanol, mp 182–185°.

Anal. Calcd for $C_{14}H_{22}Cl_2N_2O_{11}S$: C, 33.8; H, 4.43; N, 5.64. Found: C, 34.01; H, 4.47; N, 5.61.

Registry No.—**1** (X = O, m = 1, n = 3) diperchlorate, 39945-31-8; **2a**, 39945-54-5; **3a** bromide, 39945-55-6; **5a** bromide, 1449-46-3; **6a**, 772-42-9; **6a** Na salt, 39945-45-4; **6b**, 39945-46-5; **6d**, 39945-47-6; **6d** dimethylsulfonium perchlorate salt, 39945-48-7; **7a**, 39945-49-8; **8**, 39945-50-1; **11**, 39945-51-2; **12**, 39945-52-3; 3-amino-1-bromopropane, 18370-81-5; triphenylphosphine, 603-35-0; benzyl alcohol, 100-51-6.

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An Improved Synthesis of Alkyl-Substituted 1,2-Dithiolium Salts

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Although there are several convenient routes to aryl-substituted[1–4] 1,2-dithiolium ions (**3**) only two general methods have been published for the preparation of the important alkyl-substituted 1,2-dithiolium ions. Both methods depend on the action of the –S–S– group of either H_2S_x ($x \geqslant 2$)[5] or Ac–S–S–Ac[6] on the parent β-dicarbonyl compound.

In the present work, based on earlier experiments in these laboratories,[7,8] the combined action of a halogen and hydrogen sulfide on the appropriate β-dicarbonyls readily yields the corresponding 1,2-dithiolium salts (eq 1). The method requires only readily available starting materials, and, fort he 3,5-dimethyl-1,2-dithiolium ion at least, much improved yields are obtained.

With iodine as oxidant, the reaction proceeds smoothly *via* two steps. Firstly, the 1,2-dithiolium ion formed in the oxidizing medium usually separates

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[18] Prepared from α-(chloromethyl)pyrrolidine hydrochloride[19] and CbzCl.

[19] J. R. Piper and T. P. Johnston, *J. Org. Chem.*, **28**, 982 (1963).

[20] Prepared from commercially available α-(2-hydroxyethyl)piperidine and CbzCl.

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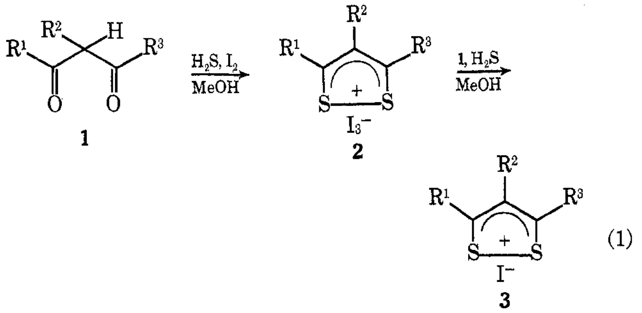

a, $R^1 = R^3 =$ Me; $R^2 =$ H
b, $R^1 =$ Me; $R^2 =$ H; $R^3 = C_6H_5$
c, $R^1 = R^2 = R^3 =$ Me
d, $R^1 = R^2 = R^3 =$ H

as its triiodide salt (**2**). This intermediate has been characterized by analysis for the 3,5-dimethyl-1,2-dithiolium ion (**2a**) only, but appears to form with the other 1,2-dithiolium ions studied. Further reaction with H_2S results in complete conversion of this intermediate to the iodide salt (**3a–c**). Bromine has been successfully used as oxidant to form the 3,5-dimethyl-1,2-dithiolium bromide (**4**). No attempt has been made to utilize chlorine as the oxidant.

Two further cations prepared in this work, *viz.*, the 3,4,5-trimethyl- (**3c**) and 3-methyl-5-phenyl-1,2-dithiolium ions (**3b**), suggest that the method may be widely applicable for the preparation of trisubstituted and aryl-substituted cations. The parent compound, 1,2-dithiolium iodide (**3d**), is not obtained from this reaction utilizing malondialdehyde tetraethyl acetal as the "β-dicarbonyl." However, this dithiolium salt has been obtained in reasonable yield from the same reaction in the presence of anhydrous HCl.[9]

Experimental Section

H_2S gas was dried by passage through anhydrous $CaCl_2$ towers. Nmr spectra were obtained at 100 MHz on approximately 0.5 *M* solutions of the salts in trifluoroacetic acid. All chemical shift values (δ, parts per million) are reported relative to internal TMS.

3,5-Dimethyl-1,2-dithiolium Iodide (3a). Method A.—Iodine (25 g) was dissolved in MeOH (AR, 150 ml) containing acetylacetone (10 g), and H_2S was passed through the stirred mixture at room temperature. The ensuing reaction was quite exothermic although cooling was not utilized. Large yellow-green crystals of the triiodide separated initially, but on continued treatment with H_2S they dissolved and were replaced by the dithiolium iodide. The crude product was collected, washed with MeOH, CS_2, and Et_2O, and recrystallized from glacial acetic acid (12 g), mp 148–150° (reported[6] mp 146–150°), nmr CH_3, 3.12 (6), H, 8.21 (1).

Anal. Calcd for $C_5H_7IS_2$: C, 23.3; H, 2.7; I, 49.2; S, 24.8. Found: C, 23.1; H, 2.8; I, 49.3; S, 24.8.

Method B.—H_2S was bubbled into a vigorously stirred solution of acetylacetone (50 g) and iodine (100 g) in MeOH (200 ml). After 2 hr the triiodide salt had crystallized out. The reaction mixture was brought to reflux and H_2S was passed for a further 2 hr. At this stage, the hot solution was decanted from the sulfur (~5 g) and diethyl ether (500 ml) was added. On cooling the solution deposited 60 g of the pure crystalline, yellow iodide salt, yield 60%.

Anal. Calcd for $C_5H_7IS_2$: C, 23.3; H, 2.7; I, 49.2; S, 24.8. Found: C, 23.5; H, 2.7; I, 48.8; S, 24.7.

3,5-Dimethyl-1,2-dithiolium Triiodide (2a).—A sample of the 3,5-dimethyl-1,2-dithiolium triiodide intermediate formed in the preparation of the iodide salt was isolated and twice recrystallized from MeOH, mp 118–120° (reported[6] mp 118–125°), nmr CH_3, 3.12 (6), H, 8.19 (1).

Anal. Calcd for $C_5H_7I_3S_2$: C, 11.7; H, 1.4; I, 74.4; S, 12.5. Found: C, 12.0; H, 1.4; I, 72.9; S, 11.9.

3,5-Dimethyl-1,2-dithiolium Bromide (4a).—Acetylacetone (6 ml) was carefully added to a solution of bromine (24 g) in methanol (100 ml) at 0°. H_2S was bubbled into this vigorously stirred mixture. After 5 min the remainder of the acetylacetone (9 ml) was added, almost completely discharging the color of the bromine. H_2S was bubbled into the solution at room temperature until the solution turned deep red (~4 hr). Stirring was continued overnight. The solution was separated from a small quantity of sulfur, and diethyl ether (300 ml) was slowly added with stirring. The crystals were collected and washed. The compound was recrystallized by dissolving the crude product in a quantity of warm methanol, filtering, and adding a fourfold excess of diethyl ether. On cooling, the solution deposited crystals (8 g, 25%) which were collected, washed, and dried, mp slowly decomposes above 160°, nmr CH_3, 3.12 (6), H, 8.19 (1).

Anal. Calcd for $C_5H_7BrS_2$: C, 28.5; H, 3.4; Br, 37.8; S, 30.4. Found: C, 28.5; H, 3.4; Br, 38.0; S, 30.6.

3-Methyl-5-phenyl-1,2-dithiolium Iodide (3b).—A solution of benzoylacetone (40 g) and iodine (51 g) in MeOH (150 ml) was stirred vigorously while H_2S was passed through at room temperature. Initially, sulfur was deposited and finally the dithiolium iodide crystallized from the solution. Addition of diethyl ether to the reaction mixture led to further recrystallization of the required compound, which was twice recrystallized from methanol (16 g), mp 127–132°, nmr CH_3, 3.18 (3), C_6H_5, 7.5–8.1 (5), H, 8.58 (1).

Anal. Calcd for $C_{10}H_9IS_2$: C, 37.6; H, 2.8; I, 39.7; S, 20.0. Found: C, 37.7; H, 2.9; I, 39.7; S, 20.2.

3,4,5-Trimethyl-1,2-dithiolium Iodide (3c).—H_2S was bubbled into a methanolic solution (150 ml) of α-methylacetylacetone (19 g) and iodine (46 g) for approximately 0.5 hr, when large crystals separated (presumed to be 3,4,5-trimethyl-1,2-dithiolium triiodide). On continued bubbling of H_2S (~2 hr) the large crystals were replaced by smaller yellow crystals. When the red coloration of the iodine was completely discharged the product was collected, washed, and recrystallized from MeOH as pale yellow crystals (15 g), mp 217–218°, nmr 3-CH_3 and 5-CH_3, 3.00 (6), 4-CH_3, 2.52 (3).

Anal. Calcd for $C_6H_9IS_2$: C, 26.5; H, 3.3; I, 46.6; S, 23.6. Found: C, 26.4; H, 3.3; I, 46.8; S, 23.7.

Registry No.—**1a**, 123-54-6; **1b**, 93-91-4; **1c**, 815-57-6; **2a**, 22372-84-5; **3a**, 22251-86-1; **3b**, 37344-00-6; **3c**, 39703-73-6; **4a**, 20365-60-0; iodine, 7553-56-2; bromine, 7726-95-6.

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Comparisons of the Reactions of Chlorine and Alkyl Hypochlorites with Aromatics in Nitromethane

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A few years ago Norman and Harvey[2] investigated the reactions of *tert*-butyl hypochlorite with several aromatic hydrocarbons. They found that these reac-

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