

A New Wittig Rearrangement of 2,2-Disubstituted 1,3-Dithianes

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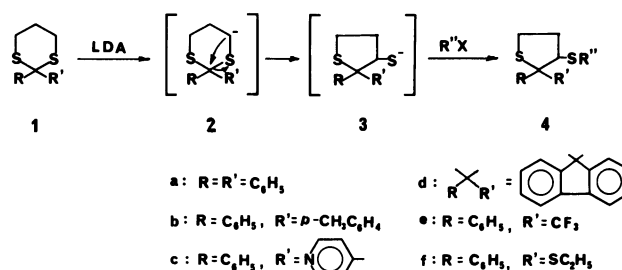
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Carbanions produced by deprotonation at the ring C-4 of 2,2-disubstituted 1,3-dithianes undergo a Wittig type rearrangement to give the anions of 2,2-disubstituted tetrahydrothiophene-3-thiols. After being trapped with several alkyl halides, these afford the corresponding 2,2-disubstituted 3-(alkylthio)tetrahydrothiophenes, which are difficult to prepare by other synthetic routes.

Recently, Wilson and his co-workers^{1,2} studied the reaction of 1,3-dithiane with anionic bases in the gas phase. They observed that it undergoes deprotonation at C-5, in competition with that at C-2. However, the deprotonation at C-5 is recognized only for 1,3-dithiane in the gas phase. In a solution, the deprotonation usually occurs at C-2. For example, 1,3-dithiane and its 2-alkyl derivatives easily undergo deprotonation at the ring C-2 by butyllithium or lithium diisopropylamide (LDA), leading to the formation of 2-lithio-1,3-dithianes.³ Many examples cited in the literature demonstrate the high nucleophilicity of the 2-lithio-1,3-dithianes as well as the utility of these reagents in synthetic organic chemistry.³ On the other hand, 2-cyclohexylidene-1,3-dithiane is deprotonated at C-4 of the 1,3-dithiane ring by butyllithium in tetrahydrofuran.⁴ The ring C-4 deprotonation has also been found by Hase and Lahtinen⁵ in the reaction of several 2-alkyl-2-trimethylsilylmethyl-1,3-dithianes with butyllithium in the presence of hexamethylphosphoric triamide, but it competes with side chain deprotonation. In most cases, the carbanion produced by deprotonation at the ring C-2 or C-4 of 1,3-dithiane and its derivatives is stable and does not undergo further transformation under the carbanion-forming conditions. In the last-mentioned reaction proposed by Hase and Lahtinen,⁵ however, the initially formed carbanion undergoes migration of trimethylsilyl group and succeeding formation of C-2 to C(α) double bond with suprafacial expulsion of S-3 as the thiolate anion under the carbanion-forming conditions. With this background, we expected that appropriate 2,2-disubstituted 1,3-dithianes should be deprotonated at C-4 by a strong base such as butyllithium or LDA. In this paper we wish to describe such a deprotonation by LDA and the behavior of the resulting anionic species, which would be made clear by trapping them by several alkyl halides.

Results and Discussion

We have studied the reactions of several 2,2-disubstituted 1,3-dithianes (**1**), such as 2,2-diaryl-1,3-dithianes (**1a**, **1b**, **1c**, and **1d**), 2-phenyl-2-trifluoromethyl-1,3-dithiane (**1e**), and 2-ethylthio-2-phenyl-1,3-dithiane (**1f**) with LDA in tetrahydrofuran in the presence or absence of *N, N, N', N'*-tetramethylethylenediamine followed by adding an appropriate alkyl halide to the reaction mixture. These reactions resulted in the high-yield formation of the corresponding 2,2-disubstituted 3-(alkylthio)tetrahydrothiophenes (**4**) after the usual



work-up procedure.

It is certain that the initial deprotonation occurred at the ring C-4 of **1**, because they possess no hydrogen at the ring C-2. Presumably, the initially formed anionic species (**2**) rearranges *via* 1,2-shift of the C-2 carrying two substituents from S-3 to C-4 as well as the simultaneous S-3 thiolate expulsion to give the anions (**3**) of 2,2-disubstituted tetrahydrothiophene-3-thiols. On trapping with alkyl halides, these afford **4**. This mechanistic interpretation reveals that the reaction is a Wittig type rearrangement involving migration of carbon from sulfur to an α -carbanion. Concerning such the rearrangement of sulfide and its homologues, to our best knowledge, only three reports have been published.^{6–8} We chose 2,2-diphenyl-3-(methylthio)-tetrahydrothiophene **4a** [$R''=\text{CH}_3$] as a representative of the obtained products **4**. We studied its ¹H-NMR spectrum in CDCl₃ by decoupling experiments involving the protons on C-3, C-4, and C-5 of **4a** [$R''=\text{CH}_3$]. It is obvious from Fig. 1 that **4a** [$R''=\text{CH}_3$] involves the $-\text{SCH}_2\text{CH}_2\text{CH}-$ system, the methylthio, and two phenyl groups. Thus, the structure of **4a** [$R''=\text{CH}_3$] should be supported by the decoupled spectra, together with the ¹³C-NMR and mass spectral data and analytical data.

This observation as well as the fact that the other products also exhibit spectral properties (¹H-NMR, ¹³C-NMR, and mass spectra) and analytical data in good accordance with the assigned structures supports the reasonableness of the above mechanistic interpretation. Also, the occurrence of this conversion was recognized only when both the substituents at C-2 of **1** are electron-withdrawing groups, suggesting that the migrating carbon may be C-2 of the 1,3-dithiane ring. All attempts to submit 2-alkyl-2-aryl- and 2,2-dialkyl-1,3-dithianes such as 2-methyl-2-phenyl-, 2-ethyl-2-phenyl-, 2,2-dimethyl-, and 2,2-diethyl-1,3-dithiane to the same deprotonation-alkylation sequence failed and resulted in the recovery of the starting 1,3-dithianes. Thus, it may be claimed that the occurrence

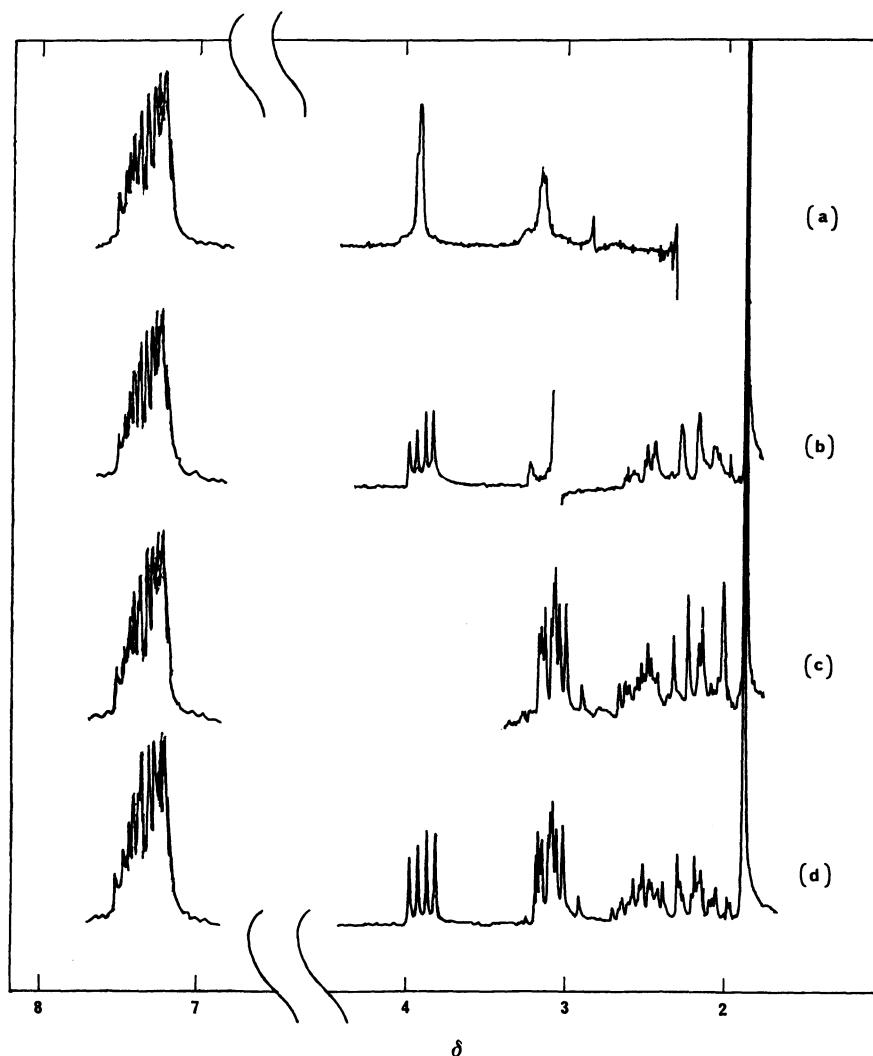


Fig. 1. The ^1H -NMR spectra of $4a[\text{R}''=\text{CH}_3]$ in CDCl_3 where (a) the protons on C-4 are decoupled, (b) the protons on C-5 are decoupled, (c) the proton on C-3 is decoupled, and (d) none of the protons is decoupled.

TABLE 1. FORMATION OF 2,2-DISUBSTITUTED 3-(ALKYLTHIO)TETRAHYDROTHIOPHENES (4) FROM 2,2-DISUBSTITUTED 1,3-DITHIANES (1)

Starting 1,3-dithiane	Trapping agent ($\text{R}''\text{X}$)	Product ^a	Yield/%	Mp $\theta_m/^\circ\text{C}$ or [Bp $\theta_b/^\circ\text{C}(\text{Torr})^\dagger$]
1a	CH_3I	4a $[\text{R}''=\text{CH}_3]$	94	75—76
1a	$\text{C}_2\text{H}_5\text{I}$	4a $[\text{R}''=\text{C}_2\text{H}_5]$	90	93—94
1a	$\text{CH}_3(\text{CH}_2)_3\text{I}$	4a $[\text{R}''=\text{CH}_3(\text{CH}_2)_3]$	93	[139 (1.5)]
1a	$\text{CH}_3(\text{CH}_2)_3\text{Br}$	4a $[\text{R}''=\text{CH}_3(\text{CH}_2)_3]$	94	
1b	CH_3I	4b $[\text{R}''=\text{CH}_3]$	92	[119 (5.5)]
1b	$\text{C}_2\text{H}_5\text{I}$	4b $[\text{R}''=\text{C}_2\text{H}_5]$	94	[135 (1.2)]
1b	$\text{CH}_3(\text{CH}_2)_3\text{I}$	4b $[\text{R}''=\text{CH}_3(\text{CH}_2)_3]$	95	[149 (1.1)]
1b	$\text{CH}_3(\text{CH}_2)_3\text{Br}$	4b $[\text{R}''=\text{CH}_3(\text{CH}_2)_3]$	76	
1c	CH_3I	4c $[\text{R}''=\text{CH}_3]$	58	133—134
1c	$\text{C}_2\text{H}_5\text{I}$	4c $[\text{R}''=\text{C}_2\text{H}_5]$	99	[128 (2.5)]
1c	$\text{CH}_3(\text{CH}_2)_3\text{I}$	4c $[\text{R}''=\text{CH}_3(\text{CH}_2)_3]$	92	[136 (4)]
1c	$\text{CH}_3(\text{CH}_2)_3\text{Br}$	4c $[\text{R}''=\text{CH}_3(\text{CH}_2)_3]$	61	
1d	CH_3I	4d $[\text{R}''=\text{CH}_3]$	90	139—140
1d	$\text{C}_2\text{H}_5\text{I}$	4d $[\text{R}''=\text{C}_2\text{H}_5]$	99	114—115
1d	$\text{CH}_3(\text{CH}_2)_3\text{I}$	4d $[\text{R}''=\text{CH}_3(\text{CH}_2)_3]$	97	— ^b
1d	$\text{CH}_3(\text{CH}_2)_3\text{Br}$	4d $[\text{R}''=\text{CH}_3(\text{CH}_2)_3]$	44	

TABLE 1. Continued

Starting 1,3-dithiane	Trapping agent (R''X)	Product ^{a)}	Yield/%	Mp $\theta_m/^\circ\text{C}$ or [Bp $\theta_b/^\circ\text{C(Torr)}^\dagger$]
1e	CH ₃ I	4e [R'' = CH ₃]	92	[132 (3)]
1e	C ₂ H ₅ I	4e [R'' = C ₂ H ₅]	80	[133 (2.5)]
1f	CH ₃ I	4f [R'' = CH ₃]	69	[133 (3)]
1f	C ₂ H ₅ I	4f [R'' = C ₂ H ₅]	91	[150 (3.5)]
1f	CH ₃ (CH ₂) ₃ I	4f [R'' = CH ₃ (CH ₂) ₃]	91	[162 (3.5)]

a) The products **4c** were isolated by column chromatography (silica gel, 25% ethyl acetate/chloroform). The other products were also isolated by column chromatography (silica gel, 10% ethyl acetate/hexane). All products listed in this table were a mixture of diastereomers. They were also characterized by mass spectra in addition to ¹H-NMR, ¹³C-NMR, and elemental analysis. b) Decomposes during distillation under reduced pressure.

† 1 Torr \approx 133.322 Pa.

TABLE 2. ¹H- AND ¹³C-NMR SPECTRA OF **4a**, **4b**, AND **4c**

Compound	¹ H-NMR (δ , CDCl ₃) ^{a)}	¹³ C-NMR (δ , CDCl ₃) ^{a)}
4a [R'' = CH ₃]	1.82(s, 3H), 2.2—2.6(m, 2H), 2.9—3.2(m, 2H), 3.8—4.0(m, 1H), 7.0—7.5(m, 10H)	15.09(q), 29.13(t), 34.46(t), 56.28(d), 68.09(s), 126.72(d), 127.01(d), 127.36(d), 128.12(d), 129.99(d), 143.21(s), 145.67(s)
4a [R'' = C ₂ H ₅]	1.15(t, 3H, $J=7$ Hz), 1.9—2.8(m, 4H), 2.9—3.2(m, 2H), 3.7—4.1(m, 1H), 7.0—7.5(m, 10H)	14.68(q), 26.27(t), 29.25(t), 35.51(t), 54.93(d), 68.09(s), 126.66(d), 126.95(d), 127.48(d), 128.06(d), 128.36(d), 129.29(d), 129.99(d), 143.33(s), 145.61(s)
4a [R'' = CH ₃ (CH ₂) ₃]	0.6—1.1(m, 3H), 1.1—1.6(m, 4H), 2.0—2.8(m, 4H), 2.9—3.2(m, 2H), 3.7—4.1(m, 1H), 7.0—7.5(m, 10H)	13.63(q), 21.94(t), 29.08(t), 31.59(t), 31.94(t), 35.45(t), 55.23(d), 68.04(s), 126.54(d), 126.83(d), 127.42(d), 127.95(d), 129.93(d), 143.27(s), 145.56(s)
4b [R'' = CH ₃]	1.79(s, 1.5H), 1.85(s, 1.5H), 2.23(s, 3H), 2.1—2.5(m, 2H), 2.8—3.2(m, 2H), 3.6—4.0(m, 1H), 6.8—7.5(m, 9H)	14.92(q), 15.05(q), 20.89(q), 28.96(t), 34.34(t), 56.22(d), 56.34(d), 67.75(s), 67.86(s), 126.48(d), 126.83(d), 127.19(d), 127.30(d), 127.65(d), 127.95(d), 128.18(d), 128.71(d), 129.93(d), 136.02(s), 136.37(s), 140.29(s), 142.69(s), 143.27(s), 145.73(s)
4b [R'' = C ₂ H ₅]	1.15(t, 3H, $J=7$ Hz), 1.9—2.8(m, 4H), 2.28(s, 3H), 2.9—3.2(m, 2H), 3.7—4.1(m, 1H), 6.9—7.5(m, 9H)	14.68(q), 20.94(q), 26.21(t), 26.33(t), 29.13(t), 35.45(t), 54.93(d), 67.75(s), 67.86(s), 126.54(d), 126.83(d), 127.24(d), 127.36(d), 127.65(d), 127.95(d), 128.71(d), 129.93(d), 136.08(s), 136.43(s), 140.35(s), 142.63(s), 143.39(s), 145.67(s)
4b [R'' = CH ₃ (CH ₂) ₃]	0.7—1.1(m, 3H), 1.1—1.7(m, 4H), 1.9—2.6(m, 4H), 2.27(s, 3H), 2.8—3.1(m, 2H), 3.5—3.9(m, 1H), 6.8—7.5(m, 9H)	13.57(q), 20.89(q), 22.06(t), 29.13(t), 29.43(t), 31.77(t), 32.12(t), 35.69(t), 55.75(d), 68.09(s), 68.21(s), 126.54(d), 126.89(d), 127.42(d), 127.54(d), 127.71(d), 127.95(d), 128.29(d), 128.71(d), 129.06(d), 129.23(d), 129.35(d), 130.05(d), 136.14(s), 136.43(s), 140.52(s), 142.81(s), 143.57(s), 145.85(s)
4c [R'' = CH ₃]	1.84(s, 1.5H), 1.90(s, 1.5H), 2.2—2.6(m, 2H), 2.9—3.2(m, 2H), 3.6—4.0(m, 1H), 7.0—7.4(m, 7H), 8.3—8.5(m, 2H)	14.98(q), 15.44(q), 29.13(t), 29.31(t), 34.28(t), 34.69(t), 55.87(d), 56.05(d), 67.22(s), 67.39(s), 122.39(d), 124.85(d), 127.30(d), 128.30(d), 129.82(d), 141.52(s), 144.09(s), 148.71(d), 149.71(d), 152.22(s), 154.51(s)
4c [R'' = C ₂ H ₅]	1.19(t, 3H, $J=7$ Hz), 2.1—2.6(m, 4H), 2.9—3.3(m, 2H), 3.7—4.1(m, 1H), 7.1—7.5(m, 7H), 8.4—8.6(m, 2H)	14.68(q), 26.33(t), 26.68(t), 29.19(t), 29.37(t), 35.57(t), 35.98(t), 54.99(d), 55.11(d), 67.45(s), 67.69(s), 122.50(d), 124.85(d), 127.24(d), 127.36(d), 127.48(d), 128.24(d), 129.88(d), 141.75(s), 144.15(s), 148.71(d), 149.65(d), 152.46(s), 154.56(s)
4c [R'' = CH ₃ (CH ₂) ₃]	0.7—1.1(m, 3H), 1.1—1.8(m, 4H), 2.1—2.7(m, 4H), 2.9—3.2(m, 2H), 3.7—4.0(m, 1H), 7.1—7.5(m, 7H), 8.3—8.5(m, 2H)	13.57(q), 21.94(t), 29.19(t), 29.37(t), 31.65(t), 32.12(t), 32.53(t), 35.57(t), 35.92(t), 55.23(d), 55.40(d), 67.45(s), 67.69(s), 122.50(d), 124.85(d), 127.13(d), 127.24(d), 127.36(d), 127.48(d), 128.24(d), 129.88(d), 141.75(s), 144.15(s), 148.71(d), 149.65(d), 152.46(s), 154.56(s)

a) Measured at 25 °C.

TABLE 3. ^1H - AND ^{13}C -NMR SPECTRA OF **4d**, **4e**, AND **4f**

Compound	^1H -NMR (δ , CDCl_3) ^a	^{13}C -NMR (δ , CDCl_3) ^a
4d [R''=CH ₃]	1.57(s, 3H), 2.4—2.8(m, 2H), 3.1—3.5(m, 2H), 3.5—3.9(m, 1H), 7.1—7.7(m, 8H)	15.97(q), 30.19(t), 37.27(t), 61.25(d), 66.05(s), 119.64(d), 123.73(d), 125.78(d), 127.30(d), 127.65(d), 128.12(d), 128.30(d), 139.88(s), 140.58(s), 148.13(s), 149.53(s)
4d [R''=C ₂ H ₅]	0.83(t, 3H, $J=7$ Hz), 1.96(q, 2H, $J=7$ Hz), 2.5—2.9(m, 2H), 3.2—3.4(m, 2H), 3.5—3.9(m, 1H), 7.1—7.8(m, 8H)	14.74(q), 26.68(t), 30.19(t), 38.20(t), 59.26(d), 65.93(s), 119.64(d), 123.67(d), 125.61(d), 127.30(d), 127.59(d), 128.06(d), 128.24(d), 139.88(s), 140.69(s), 147.95(s), 149.65(s)
4d [R''=CH ₃ (CH ₂) ₃]	0.5—0.8(m, 3H), 0.8—1.3(m, 4H), 1.8—2.1(m, 2H), 2.5—2.9(m, 2H), 3.2—3.5(m, 2H), 3.5—3.9(m, 1H), 7.1—7.7(m, 8H)	13.46(q), 21.47(t), 30.19(t), 31.65(t), 32.35(t), 38.14(t), 59.38(d), 65.93(s), 119.58(d), 119.70(d), 123.67(d), 125.61(d), 127.30(d), 127.59(d), 128.06(d), 128.24(d), 139.94(s), 140.70(s), 147.95(s), 149.65(s)
4e [R''=CH ₃]	1.80(s, 3H), 1.9—2.7(m, 2H), 1.7—3.2(m, 2H), 3.5—3.8(m, 1H), 7.0—7.3(m, 3H), 7.3—7.7(m, 2H)	15.44(q), 30.13(t), 36.15(t), 55.46(d), 121.80(s), 127.48(d), 128.06(d), 128.41(d), 130.05(d), 130.17(d), 133.09(s), 135.02(s)
4e [R''=C ₂ H ₅]	1.11(t, 1.5H, $J=7$ Hz), 1.23(t, 1.5H, $J=7$ Hz), 2.35(q, 1H, $J=7$ Hz), 2.50(q, 1H, $J=7$ Hz), 2.2—2.7(m, 2H), 2.9—3.3(m, 2H), 3.7—3.9(m, 1H), 7.1—7.4(m, 3H), 7.4—7.7(m, 2H)	14.45(q), 26.33(t), 30.13(t), 37.21(t), 53.41(d), 121.86(s), 127.42(d), 128.00(d), 128.30(d), 128.47(d), 130.11(d), 135.26(s)
4f [R''=CH ₃]	1.04(t, 3H, $J=7$ Hz), 1.0—1.7(m, 1H), 1.86(s, 3H), 2.47(q, 2H, $J=7$ Hz), 2.0—2.9(m, 2H), 2.9—3.7(m, 2H), 7.0—7.4(m, 3H), 7.5—7.8(m, 2H)	13.46(q), 15.50(q), 26.15(t), 29.25(t), 35.34(t), 61.54(d), 77.22(s), 127.36(d), 128.06(d), 128.36(d), 129.29(d), 140.70(s)
4f [R''=C ₂ H ₅]	1.05(t, 3H, $J=7$ Hz), 1.10(t, 3H, $J=7$ Hz), 2.32(q, 4H, $J=7$ Hz), 2.0—3.8(m, 5H), 7.0—7.3(m, 3H), 7.5—7.8(m, 2H)	13.39(q), 14.68(q), 26.13(t), 29.18(t), 35.99(t), 59.24(d), 76.91(s), 127.22(d), 129.16(d), 140.67(s)
4f [R''=CH ₃ (CH ₂) ₃]	0.6—1.0(m, 3H), 1.05(t, 3H, $J=7$ Hz), 1.1—1.7(m, 4H), 2.38(q, 2H, $J=7$ Hz), 2.1—3.8(m, 7H), 7.0—7.4(m, 3H), 7.5—7.7(m, 2H)	13.39(q), 13.56(q), 21.84(t), 26.18(t), 29.24(t), 31.59(t), 31.99(t), 36.11(t), 59.65(d), 77.08(s), 127.28(d), 129.22(d), 140.73(s)

a) Measured at 25 °C.

TABLE 4. ANALYTICAL DATA OF 2,2-DISUBSTITUTED 3-(ALKYLTHIO)TETRAHYDROTHIOPHENES (**4**)

Compound	Found/%			Calcd/%		
	C	H	N	C	H	N
4a [R''=CH ₃]	71.03	6.26		71.28	6.33	
4a [R''=C ₂ H ₅]	71.98	6.52		71.95	6.71	
4a [R''=CH ₃ (CH ₂) ₃]	73.04	7.25		73.11	7.36	
4b [R''=CH ₃]	71.89	6.67		71.95	6.71	
4b [R''=C ₂ H ₅]	72.54	7.05		72.56	7.05	
4b [R''=CH ₃ (CH ₂) ₃]	73.65	7.61		73.63	7.65	
4c [R''=CH ₃]	66.80	5.89	4.82	66.85	5.96	4.87
4c [R''=C ₂ H ₅]	67.66	6.25	4.53	67.73	6.35	4.65
4c [R''=CH ₃ (CH ₂) ₃]	69.22	6.95	4.10	69.25	7.04	4.25
4d [R''=CH ₃]	71.74	5.59		71.78	5.67	
4d [R''=C ₂ H ₅]	72.33	6.00		72.43	6.08	
4d [R''=CH ₃ (CH ₂) ₃]	73.59	6.72		73.57	6.79	
4e [R''=CH ₃]	51.66	4.68		51.78	4.71	
4e [R''=C ₂ H ₅]	53.31	4.95		53.40	5.17	
4f [R''=CH ₃]	57.67	6.61		57.73	6.71	
4f [R''=C ₂ H ₅]	59.05	7.05		59.10	7.09	
4f [R''=CH ₃ (CH ₂) ₃]	61.24	7.66		61.48	7.74	

of this conversion requires the presence of two electron-withdrawing groups at C-2 of the 1,3-dithiane ring. Although this method is applicable only to the above-mentioned 2,2-disubstituted 1,3-dithianes such as **1**, the mild conditions required and high yields of the objective **4**, as can be seen in Table 1, make this method valuable. Tables 2 and 3 give ^1H - and ^{13}C -NMR spectral data of **4a**—**c** and **4d**—**f**, respectively. The analytical data of **4** are listed in Table 4.

Experimental

All 2,2-disubstituted 1,3-dithianes (**1a**, **1b**, **1c**, **1d**, and **1e**) employed in this research were prepared by the AlCl_3 -catalyzed reaction of the corresponding ketones with 1,3-propanedithiol. The compound **1f** was prepared from 2-lithio-2-phenyl-1,3-dithiane generated by the known method and diethyl disulfide in tetrahydrofuran at low temperature. Tetrahydrofuran and N,N,N',N' -tetramethylethylenediamine were dried over lithium aluminium hydride and calcium hydride respectively, and then distilled prior to use. The other reagents were commercially available and were used without further purification.

Reactions Summarized in Table 1. To lithium diisopropylamide (LDA), prepared from diisopropylamine (0.35 g, 3.5 mmol) in tetrahydrofuran (7 ml) and 1.56 molar solution (2.12 ml, 3.3 mmol) of butyllithium in hexane, was added a solution of **1** (1.3 mmol) in tetrahydrofuran (4 ml) with stirring at -78°C . Only when **1a** and **1b** were used as the dithiane component N,N,N',N' -tetramethylethylenediamine (0.41 g, 3.5 mmol) was added⁹⁾ prior to the addition of **1**. The reaction mixture was allowed to warm to -15°C and the stirring was continued for 1 h at the same temper-

ature. The mixture was cooled again to -78°C , and an appropriate alkyl halide (3.3 mmol) was added with stirring. The stirring was continued for 1 h at -10 — -5°C and for 24 more hours at room temperature. The reaction mixture was quenched with water (100 ml) and a saturated aqueous solution (20 ml) of ammonium chloride, and then extracted with diethyl ether (3 \times 60 ml). The combined ethereal extracts were dried over anhydrous magnesium sulfate and concentrated *in vacuo* to give a pale yellow residue, which was subjected to column chromatography on silica gel. The eluents used for the column chromatography are indicated as the marginal notes of Table 1.

References

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