

## Preparation and Mass Spectra of 2,5-Diaryl-1,4-dithiins

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Received February 25, 1972

Seven 2,5-diaryl-1,4-dithiins were prepared from phenacyl halides *via* the corresponding Bunte salts. The mass spectra showed a number of similarities within this series of compounds. Various dipositive ions were observed in all cases while the unsubstituted and *p*-methyl derivatives formed tripositive ions. Ir, nmr, and chemical analysis were also completed and reported.

Several 2,5-diaryl-1,4-dithiins (**2**) (**1**) were prepared to investigate the intermolecular interactions of this heterocyclic ring system, which preferentially exists in a boat conformation (**2**). The dithiins were prepared essentially by the method of Baker and Barkenbus (**3**), which involves hydrolysis of the Bunte salts,  $\text{ArCOCH}_2\text{SSO}_3\text{Na}$ , followed by self-condensation of the resultant phenacyl mercaptans. Except for *p*-methylphenacyl bromide, the phenacyl bromides required for the preparation of the Bunte salts were commercial products, which were recrystallized prior to use. *p*-Methylphenacyl bromide was prepared from *p*-methylacetophenone by the method of Kindler and Blaas (**4**), and recrystallized from dilute alcohol.

Data on the preparation and properties of the dithiins (**2**) are given in Table I.

The infrared spectra of the compounds were consistent with the assigned structures. All derivatives showed aromatic C-H stretching at 3.2 to 3.3  $\mu$  and the expected aromatic patterns in the 6 to 7 and 8 to 10  $\mu$  range.

The aromatic out-of-plane bands at 11.6 to 12.5  $\mu$  for **2** adjacent hydrogens and above 13  $\mu$  for 5 adjacent hydrogens were observed. Other pronounced absorption bands were the aromatic ether band at 8.3  $\mu$  for **2** ( $Z = \text{OCH}_3$ ) and the aromatic nitro band at 7.4  $\mu$  for **2** ( $Z = \text{NO}_2$ ).

Table II contains the nmr data for the various dithiins, except for the *p*-nitro and *p*-phenyl derivatives for which no suitable solvent was found. It would appear that the substituent phenyl rings are rotating with respect to the dithiin nuclei. The analysis of this rotation as a function of solvent and temperature is presently under investigation.

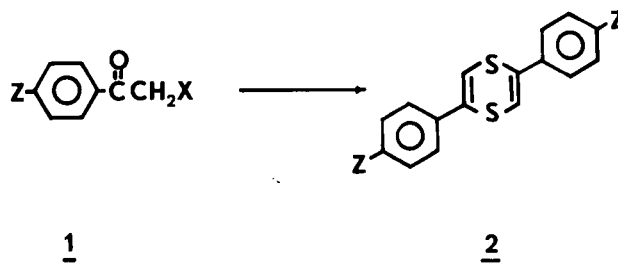


TABLE I  
2,5-Diaryl-1,4-dithiins (**2**)

Z	Color	% Yield	M.p., °C	Formula	% C		% H	
					Calcd.	Found	Calcd.	Found
H	yellow	75	116-117	$\text{C}_{16}\text{H}_{12}\text{S}_2$	71.60	71.78	4.51	4.69
$\text{CH}_3$	yellow	50	136-137	$\text{C}_{18}\text{H}_{16}\text{S}_2$	72.93	73.12	5.44	5.64
Cl	yellow	71	150-151	$\text{C}_{16}\text{H}_{10}\text{Cl}_2\text{S}_2$	56.99	56.82	2.99	3.39
Br	yellow	67	159-160	$\text{C}_{16}\text{H}_{10}\text{Br}_2\text{S}_2$	45.09	45.37	2.37	2.67
$\text{NO}_2$	reddish-orange	38	214-215	$\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_4\text{S}_2$	53.62	53.71	2.81	2.69
$\text{CH}_3\text{O}$	yellow	45	136-137	$\text{C}_{18}\text{H}_{16}\text{O}_2\text{S}_2$	65.83	65.59	4.91	5.24
$\text{C}_6\text{H}_5$	yellow or orange	65	285-287	$\text{C}_{28}\text{H}_{20}\text{S}_2$	79.99	80.27	4.80	4.81

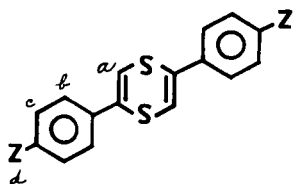


Figure 1 is a computer replication of the mass spectral data of the parent compound, 2,5-bisphenyl-1,4-dithiin. Peaks corresponding to ions of relatively low abundance (less than 3% of the base peak) were omitted. The program normalized and plotted the mass spectrum from raw data on punch cards and thus gave permanent records of the mass spectra. Mass spectral data of the derivatives are given in the Experimental section.

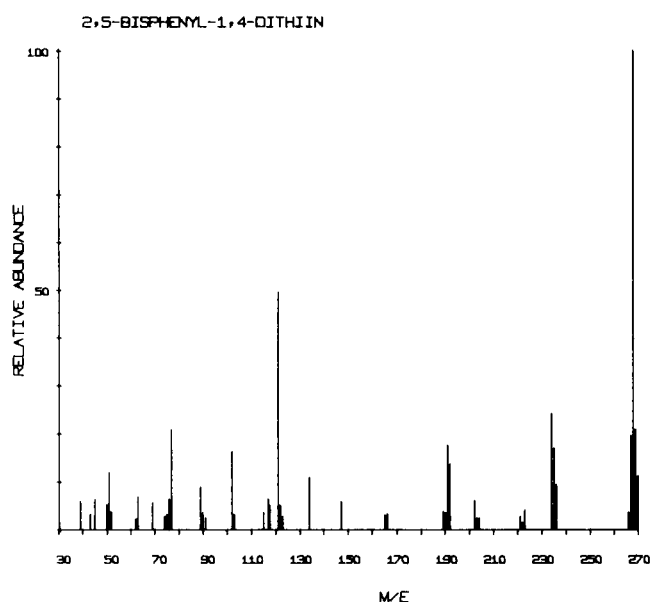


Figure 1. Mass spectrum of 2,5-Bisphenyl-1,4-dithiin.

TABLE II

Nmr Data of Dithiins (2)

Z	$\tau$	
H	a = 3.62	b,c,d = multiplet centered at ca. 2.6
Cl	a = 3.58	b,c = AB quartet at 2.46, 2.60, 2.73, 2.86 J <sub>bc</sub> = 9.5 cps
Br	a = 3.56	b,c = singlet at 2.61
CH <sub>3</sub>	a = 3.67	b,c = AB quartet at 2.56, 2.68, 2.90, 3.02 J <sub>bc</sub> = 8.0 cps d = singlet at 7.68
OCH <sub>3</sub>	a = 3.74	b,c = AB quartet at 2.51, 2.67, 3.18, 3.33 J <sub>bc</sub> = 9.0 cps d = singlet at 6.26

The parent ions were the base peaks in the spectra of all dithiins tested, accounting for 20-25% of the total ion current. The unfragmented molecules were thus remarkably stable. The dithiin ring may of course be broken without fragmentation. The parent ions exhibited the expected distribution corresponding to C-13, S-34 and halogen isotopes.

All dithiins showed peaks corresponding to loss of H ( $M-1$ )<sup>+</sup>, although those in the spectra of the nitro and bromo derivatives were very small. Metastable peaks corresponding to H ejection were present in most spectra. The nitro-substituted dithiin showed the NO ejection-rearrangement ion ( $M-NO$ )<sup>+</sup>. All dithiins showed ( $M-S$ )<sup>+</sup> peaks. The peak in the spectrum of the *p*-phenyl derivative was especially intense while that of the *p*-bromo derivative was weak. The dithiins, except the *p*-bromo and *p*-nitro derivatives, exhibited peaks corresponding to ( $M-HS$ )<sup>+</sup> and ( $M-H_2S$ )<sup>+</sup> with broad metastable peaks corresponding to the latter fragmentation.

Positive ions remaining after removal of one of the para substituents ( $M-Z$ )<sup>+</sup> were observed in the spectra of all dithiins tested, as well as ions remaining after elimination of HZ. The loss of CH<sub>3</sub>OH from the methoxy derivative was of course indistinguishable from S elimination. Ions with mass number 266, which could result from the elimination of both Z groups, were present in all dithiin spectra and were fairly intense from the halo derivatives.

Ions resulting from the concurrent elimination of Z and S were weak or absent but the ions ( $M-HZS$ )<sup>+</sup> were present in all spectra. Ions remaining by elimination of both sulfur atoms were weak or absent.

Ions remaining after elimination of one substituted benzene ring ( $M-ZC_6H_4$ )<sup>+</sup> were observed in all spectra in the expected isomer distribution. These peaks were intense in the spectra of the unsubstituted, halo, and methyl derivatives.

Positive ions corresponding to ( $ZC_6H_4CS$ )<sup>+</sup> and ( $ZC_6H_4C_2H$ )<sup>+</sup> which included a part of the dithiin ring and which were probably analogous to the tropylium ion were observed in all spectra. Ions possibly corresponding to ( $C_6H_4CS$ )<sup>+</sup> (mass number 120) were present in the spectra of the halo and nitrosubstituted derivatives.

Dipositive ions  $M^{2+}$  were present in all dithiin spectra, as judged by the peaks at half mass numbers resulting from ions containing C-13. As judged from the relative intensities of the  $M/2$  and  $(M+1)/2$  peaks, the species ( $M/2$ )<sup>+</sup> appeared to be present also but this point could not be definitely established. Very small  $M^{+3}$  peaks appeared in the unsubstituted (89 1/3) and *p*-methyl (98 2/3) derivatives. Dipositive ions were also observed in several examples corresponding to ( $M-S$ )<sup>2+</sup>, ( $M-H_2S$ )<sup>2+</sup>, ( $M-Z$ )<sup>2+</sup> and ( $M-2Z$ )<sup>2+</sup>.

Several peaks of small fragments were observed in all

spectra, specifically those with mass number 89 ( $C_7H_5^+$ ), 76 ( $C_6H_4^+$ ) (also 77 in the unsubstituted derivative), 75 ( $C_6H_3^+$ ), 69 ( $HC_3S^+$ ), 63 ( $C_5H_3^+$ ), 51 ( $C_4H_3^+$ ), 50 ( $C_4H_2^+$ ), 45 ( $HCS^+$ ), and 39 ( $C_3H_3^+$ ).

Several metastable transition peaks were present in the spectra and these were attributed to the following ion transformations:  $M^+ \rightarrow (M-H)^+$  (all spectra),  $M^+ \rightarrow (M-HS)^+$  (unsubstituted, *p*-methyl),  $M^+ \rightarrow (M-Cl)^+$  (*p*-chloro),  $M^+ \rightarrow (M-Br)^+$  (*p*-bromo),  $(M-Br)^+ \rightarrow (M-2Br)^+$  (*p*-bromo),  $M^+ \rightarrow (M-CH_3)^+$  (*p*-methyl and *p*-methoxy), and  $M^+ \rightarrow (M-CH_3O)^+$  (*p*-methoxy).

### EXPERIMENTAL

#### Sodium Phenacyl Thiosulfates.

A mixture of 0.10 mole of the phenacyl bromide and 0.10 mole of sodium thiosulfate pentahydrate in 200 ml. of 50 to 70% alcohol was stirred and heated gently for 30 minutes to 1 hour. The alcohol was allowed to evaporate during this time. The mixture was then chilled in an ice bath and the product was collected by filtration. The Bunte salts,  $p-ZC_6H_4COCH_2S_2O_3Na$  ( $Z = H, CH_3, CH_3O, Cl, Br, NO_2, C_6H_5$ ), were obtained in analytical pure, anhydrous form in 85-95% yield, by drying to constant weight at 60°. Moist samples can be used in the succeeding step.

#### Dithiins.

The sodium phenacyl thiosulfate (0.100 mole) was dissolved in a solution of 150 ml. of water, 150 ml. of acetic acid, and 75 ml. of concentrated hydrochloric acid and the resultant solution was refluxed for 4 hours. With the *p*-phenyl derivative, an additional 150 ml. of acetic acid was added during the reflux period. The mixtures were recrystallized from acetic acid except the *p*-phenyl derivative, which was sparingly soluble in the usual organic solvents. It was obtained in an orange form from ethylene bromide or in a yellow form from large quantities of chloroform. The *p*-nitro derivative could also be crystallized from acetone.

#### Nmr and Ir Spectra.

Nmr spectra were recorded with a Varian A-60A spectrometer at 36.5° in Mallinckrodt spectrograde carbon disulfide. Tetramethylsilane (TMS) was added as an internal standard. All compounds with the exception of 2,5-bis-*p*-nitrophenyl-1,4-dithiin and 2,5-bis-*p*-biphenyl-1,4-dithiin were soluble enough in carbon disulfide to give a satisfactory spectrum.

Infrared spectra of the dithiins in potassium bromide discs were taken with a Beckman IR-4 spectrophotometer.

#### Mass Spectra.

Mass spectra were obtained with a Hitachi RMU-6E mass spectrometer. All samples were introduced by means of a direct insertion probe. The chamber temperature was approximately 110 to 120° except for the *p*-nitro ( $\cong 160^\circ$ ) and *p*-phenyl ( $\cong 200^\circ$ ) derivatives. The sample heater was 100° or less. The ionizing voltage was set at 80 eV with a total emission current of 80  $\mu A$  for all samples.

The principal ions in the mass spectrum of 2,5-bisphenyl-1,4-dithiin were (*m/e* and abundance relative to the base peaks listed): 270, 11.2; 269, 20.9; 268, 100.0; 267, 19.6; 236, 9.4; 235, 17.0; 234, 24.2; 202, 6.1; 192, 13.7; 191, 17.6; 147, 5.8; 134,

10.9; 122, 5.1; 121, 49.6; 117.5, 5.1; 117, 6.4; 102, 16.3; 89, 8.9; 77, 20.9; 76, 6.4; 69, 5.6; 63, 6.9; 51, 12.0; 50, 5.3; 45, 6.4; 39, 5.8. Metastable transition peaks were observed at 267, 234, 206, 190, and 137.5 *m/e*.

2,5-Bis(*p*-tolyl)-1,4-dithiin showed the following principal ions (*m/e* and relative abundance listed): 298, 11.0; 297, 22.9; 296, 100.0; 295, 9.6; 281, 10.9; 264, 9.4; 263, 7.6; 262, 5.7; 248, 18.8; 205, 14.3; 135, 28.0; 134, 7.0; 116, 8.0; 115, 21.4; 91, 13.5; 89, 6.5; 65, 7.8; 63, 6.5; 45, 5.7; 39, 6.5. Metastable transition peaks at *ca.* 295, 266.5, and 234 were present.

Similar data for the other dithiins are listed. 2,5-Bis(*p*-methoxyphenyl)-1,4-dithiin principal ions: 330, 11.9; 329, 22.2; 328, 100.0; 313, 19.8; 297, 7.4; 296, 21.5; 281, 11.0; 237, 12.6; 164, 8.3; 151, 17.7; 149, 5.2; 136, 5.4; 132, 14.1; 117, 9.0; 108, 7.2; 89, 14.9; 77, 5.9; 63, 7.8; 45, 5.7; 39, 5.3. Metastable transition peaks: 327.5, 312.5, 298.5, 267, and 223 *m/e*.

2,5-Bis(*p*-chlorophenyl)-1,4-dithiin principal ions: 340, 17.6; 339, 15.2; 338, 75.4; 337, 23.0; 336, 100.0; 306, 7.3; 304, 12.1; 303, 10.3; 302, 9.7; 301, 22.4; 300, 10.6; 270, 10.3; 268, 26.7; 267, 8.8; 266, 40.9; 227, 12.1; 225, 33.3; 189, 7.6; 168, 9.7; 157, 21.2; 155, 54.5; 138, 7.9; 136, 24.2; 134, 7.9; 133, 11.2; 132, 11.5; 120, 10.9; 111, 12.4; 101, 13.6; 89, 15.8; 75, 22.1; 69, 10.3; 63, 8.8; 51, 11.5; 50, 8.2; 45, 11.5. Metastable transition peaks: 336.5, 270, and 235 *m/e*.

2,5-Bis(*p*-bromophenyl)-1,4-dithiin principal ions: 429, 11.3; 428, 57.6; 427, 20.4; 426, 100.0; 425, 11.3; 424, 50.0; 347, 14.8; 345, 13.4; 314, 11.3; 312, 10.6; 271, 15.0; 269, 17.1; 267, 15.7; 266, 71.5; 201, 26.6; 199, 26.4; 189, 12.2; 182, 12.7; 180, 13.2; 165, 10.2; 133, 32.4; 132, 11.8; 121, 12.3; 120, 43.0; 101, 37.0; 89, 23.4; 76, 9.7; 75, 30.1; 74, 10.2; 69, 12.0; 63, 10.6; 51, 18.3; 50, 10.6; 45, 11.3. Metastable transition peaks: 425, 281.5, and 205.5 *m/e*.

2,5-Bis(*p*-nitrophenyl)-1,4-dithiin principal ions: 360, 11.8; 359, 20.0; 358, 100.0; 328, 9.3; 326, 12.5; 312, 10.7; 311, 6.8; 279, 6.4; 266, 17.5; 265, 10.4; 264, 7.1; 234, 7.8; 233, 7.1; 232, 8.2; 221, 14.3; 190, 6.4; 189, 12.8; 166, 5.0; 149, 7.8; 121, 8.6; 120, 15.0; 101, 6.8; 89, 11.4; 76, 5.7; 75, 11.1; 69, 8.2; 66, 5.0; 64, 51.4; 63, 8.2; 51, 9.6; 45, 8.6; 44, 17.8; 41, 6.4; 39, 8.2. Metastable transition peaks: 357.5 and 273 *m/e*.

2,5-Bis(*p*-biphenyl)-1,4-dithiin principal ions: 422, 14.6; 421, 33.8; 420, 100.0; 419, 7.8; 418, 6.6; 390, 6.3; 389, 21.2; 388, 62.8; 387, 6.8; 386, 8.8; 344, 7.0; 343, 8.5; 310, 6.1; 210.5, 3.4; 210, 12.9; 197, 26.3; 194.5, 5.4; 194, 19.0; 193.5, 8.5; 193, 4.6; 179, 5.6; 178, 17.8; 177, 5.4; 176, 7.5; 165, 10.5; 152, 14.6; 151, 6.1; 149, 5.8; 77, 6.0; 76, 4.3; 63, 5.4; 51, 6.8; 45, 5.4; 39, 6.3; 34, 13.1; 33, 5.4. Metastable transition peak: 418.5 *m/e*.

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