Diazepines. III. Synthesis of 4*H*-Pyrrolo[1,2-*a*]thieno[3,2-*f*][1,4]diazepines (1)

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The synthesis of 4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*][1,4]diazepines (**8**) is described. Phthalimidomethylfurans **1** were treated with bromine-methanol to give the dihydrofurans **2**, which were hydrolyzed and then hydrogenated over Raney nickel or with zinc-acetic acid to afford the 1,4-diketones **5**. Condensation of 2-amino-3-benzoylthiophenes **6** with **5** gave 3-benzoyl-2-pyrrolylthiopenes **7**. The removal of the phthaloyl group from **7** with hydrazine hydrate and ring closure to the diazepine ring yielded the new heterocycles **8**.

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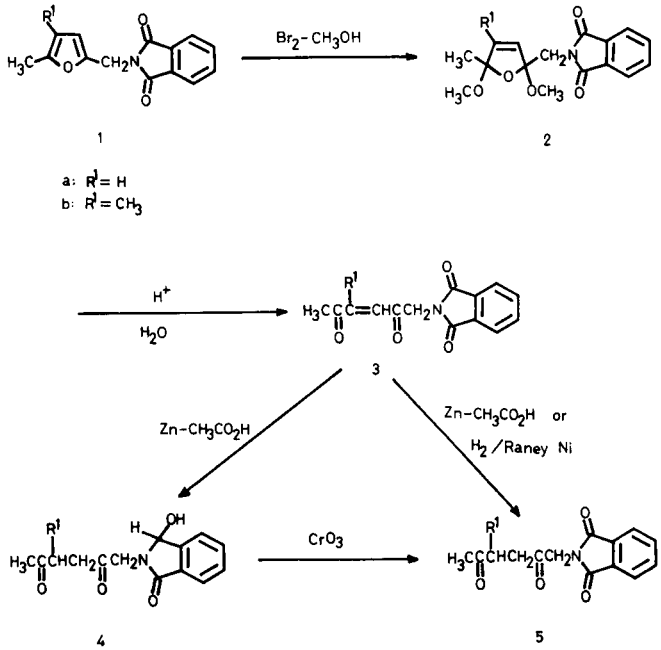
In recent years considerable attention has been drawn to the synthesis of tricyclic diazepine compounds having activity on the central nervous system (3,4). We have previously reported the synthesis of 4*H*-pyrrolo[1,2-*a*]-[1,4]benzodiazepines (1). In our continued interest in synthesis of medicinally useful diazepine compounds we have synthesized 4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*][1,4]diazepines (**8**), a heterocyclic system not yet recorded in the literature.

Scheme I



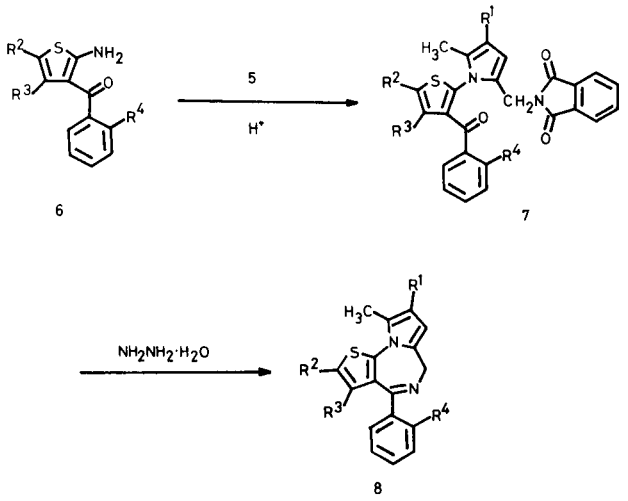
In Scheme I is shown the synthetic sequence leading to the 1,4-diketones **5**, the key intermediates for the synthesis of **8**. The dihydrofuran **2b** was prepared similarly as in the case of **2a** (1) (Scheme I). Compound **2b** was obtained as a mixture of *trans*- and *cis*-isomers as evidenced by two sets of nmr signals for the methyl and methoxy groups. The isomers were, for unambiguous structure determination, separated by fractional recrystallization from methylene chloride-*n*-hexane.

The hydrolysis of **2** in methylene chloride with hydrochloric acid or sulfuric acid at room temperature afforded **3**. The reduction of **3** to **4** was effected by zinc-acetic acid at 0-5° or hydrogenation over Raney nickel at room temperature. When **3a** was treated with zinc-acetic acid (11.4 equivalents of zinc) at the refluxing temperature for 0.5 hour, the nmr and ir spectra of the product indicated that one of the carbonyl groups was, in addition to the C-C double bond, reduced to a carbinol. The nmr signal pattern and the chemical shifts of the protons of the moiety $CH_3COCH_2CH_2CO$- were essentially the same as those of **5a** (see Experimental). A broad singlet of 1H at δ 4.1-4.6 (deuteriochloroform) and a multiplet of 1H at δ 5.83 were interpreted due to OH and C*H*OH, respectively. In the ir spectrum (potassium bromide) there was observed an absorption at 3350 cm^{-1} (OH). Based on these data the structure **4** was assigned to the reduction product, which then could be converted to **5a** with chromium trioxide. When 6.6 equivalents of zinc was

used at 2° for 1.5 hours and then at room temperature for 0.5 hour, a mixture of **5a** and **4** (in 3:2 ratio from the nmr data) was obtained. Treatment of **3a** with zinc (2.0 equivalents)-acetic acid at 2° for 75 minutes afforded **5a** in 97% yield.

Compounds 2-amino-3-benzoylthiophenes **6** were heated with **5** in benzene with *p*-toluenesulfonic acid as the catalyst to give the 3-benzoyl-2-pyrrolylthiophenes **7** (Scheme II).

Scheme II



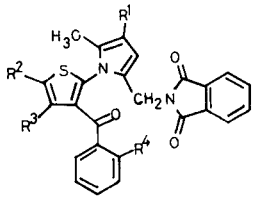
The removal of the phthaloyl group from **7** and ring closure to the diazepine ring was effected by refluxing a solution of **6** in ethanol or in a mixture of ethanol and *N*,*N*-dimethylformamide with hydrazine hydrate. The pyrrolothienodiazepines **8** gave satisfactory elemental analyses and spectral properties in respect of the ir, nmr, and mass spectra. In the nmr spectra (deuteriochloroform) of **8** the signals of CH_2N appeared as an AB-pattern (AB-quartet, but in the case of **1b** two broad singlets), whereas the corresponding methylene groups of **7** showed a singlet. Another characteristic of the nmr spectral change going from **7** to **8** is the farily large down-filed shift of the C-2′ (**7**) [C-1 (**8**)] methyl proton signal (deuteriochloroform) [from δ 2.02 (**7a**) to 2.30 or 2.42 (**8a**) and from 2.05 (**7b**) to 2.47 (**8b**)]. This is due to the anisotropic deshielding effect of the thiophene ring on the C-1 methyl protons because of the rigidity and the planality of the fused tricyclic ring system. The mass spectra at 70 eV of **8** all exhibited the large molecular ion signal and the base peak at M-15.

EXPERIMENTAL

Melting points were obtained on a Yanagimoto hot-stage apparatus and are uncorrected. Infrared spectra were recorded on a Hitachi EPI-510 spectrophotometer. Nmr data were obtained at 100 MHz on a JEOL JNM-MH-100 spectrometer unless

Table I

3-Benzoyl-2-(pyrrol-1-yl)thiophenes (**7**)



No.	R^1	R^2	R^3	R^4	M.p. °C (a)	Yield (%) (b)	Formula	*Anal.*	C (%)	H (%)	N (%)	S (%)
7a	H	CH_3	CH_3	H	161.5-162.5	86	$C_{27}H_{22}N_2O_3S$	Calcd.	71.35	4.88	6.16	7.05
								Found	71.34	4.90	5.79	6.90
7b	H	C_2H_5	H	H	145-146	83	$C_{27}H_{22}N_2O_3S$	Calcd.	71.35	4.88	6.16	7.05
								Found	71.10	4.78	5.79	7.09
7c	CH_3	CH_3	CH_3	H	175.5-176	81	$C_{28}H_{24}N_2O_3S$	Calcd.	71.77	5.16	5.98	6.84
								Found	71.92	5.05	5.68	6.63
7d	CH_3	CH_3	CH_3	Cl	175-176	80	$C_{28}H_{23}ClN_2O_3S$	Calcd.	66.86	4.61	5.57	6.37
								Found	66.56	4.54	5.45	6.16
7e	H	CH_3	CH_3	Cl	176-177	85	$C_{27}H_{21}ClN_2O_3S$	——	(c)			

(a) Recrystallization solvent; methylene chloride-*n*-hexane. (b) Yield after recrystallization. (c) Not analyzed, but satisfactory mass spectral data were obtained (see Table II).

otherwise noted, and chemical shifts are reported in parts per million (δ) with tetramethylsilane as an internal standard. Mass spectra were run on a LKB 9000 spectrometer at 70 eV.

2,3-Dimethyl-5-phthalimidomethylfuran (**1b**).

4,5-Dimethylfurfurylamine was prepared from 4,5-dimethylfurfural (5) by the procedure employed by Mndzhoyan for making 5-methylfurfurylamine from 5-methylfurfural (6). 4,5-Dimethylfurfurylamine (4.0 g., 32 mmoles) so obtained was heated with phthalic anhydride (6.3 g., 32 mmoles) in an oil bath of 130° for 1 hour. The material which solidified itself on cooling was recrystallized from ethanol to give colorless crystals (6.3 g., 77%), m.p. 122-123°. An additional recrystallization gave analytical sample, m.p. 123-124°, ir (potassium bromide): 1775, 1728, 1614, 1570 cm^{-1}; nmr (deuteriochloroform): δ 1.84 (3H, s, 4-CH_3), 2.11 (3H, s, 5-CH_3), 4.74 (2H, s, CH_2), 6.17 (1H, s, 3-H), 7.60-8.00 (4H, m, C_6H_4).

Anal. Calcd. for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.48. Found: C, 70.47; H, 5.10; N, 5.50.

2,5-Dimethoxy-2,3-dimethyl-5-phthalimidomethyldihydrofuran (**2b**).

A solution of bromine (1.7 g., 10.5 mmoles) in a mixture of dry methylene chloride (4 ml.) and absolute methanol (2 ml.) was added with stirring over 20 minutes to a solution of **1b** (2.55 g., 10.0 mmoles) in a mixture of dry methylene chloride (40 ml.) and absolute methanol (4 ml.) at -40~-50°. After stirring at this temperature for an additional 30 minutes the mixture was made alkaline by bubbing ammonia. The generated solid was filtered off, and the filtrate was washed with water and aqueous sodium chloride solution, and dried over anhydrous sodium sulfate with added benzyltrimethyl ammonium hydroxide (0.1 ml.). The oil obtained on evaporation of the solvent was crystallized with ether. The crude product was recrystallized from methylene chloride-*n*-hexane to give a mixture of *cis*- and *trans*-isomers as colorless crystals (2.77 g., 80%); ir (potassium bromide): 1770, 1720, 1384 cm^{-1}; nmr (deuteriochloroform) (7): δ 1.25, 1.50, and 1.69 (6H, each s, 2 x CH_3), 3.12, 3.21, 3.27, and 3.35 (6H, each s, 2 x OCH_3), 3.99 (2H, s, CH_2N), 5.52 (1H, m, 3-H), 7.5-8.0 (4H, m, C_6H_4). The mixture of the stereoisomers was recrystallized three times from methylene chloride-*n*-hexane to afford a single isomer, m.p. 104-105°; nmr (deuteriochloroform): δ 1.46 (3H, s, CH_3), 1.64 (3H, s, CH_3), 3.09 (3H, s, OCH_3), 3.18 (3H, s, OCH_3), 3.96 (2H, s, CH_2N), 5.49 (1H, m, 3-H), 7.6-7.9 (4H, m, C_6H_4).

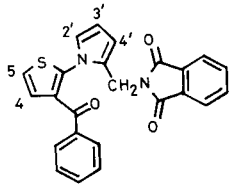
Anal. Calcd. for $C_{17}H_{19}NO_5$: C, 64.34; H, 6.03; N, 4.41. Found: C, 64.12; H, 5.77; N, 4.66.

1-Phthalimidohex-3-en-2,5-dione (**3a**).

Twelve *N* sulfuric acid (0.1 ml.) was added to a solution of 2,5-dimethoxy-2-methyl-5-phthalimidomethyldihydrofuran (**2a**) (500 mg., 1.65 mmoles) in methylene chloride. After stirring at room temperature for 2 hours, the mixture was made alkaline with saturated aqueous sodium bicarbonate solution. The layers were separated, and the organic layer was washed with aqueous sodium chloride solution and dried over anhydrous sodium sulfate. The crude product obtained on evaporation of the solvent was recrystallized from methylene chloride-*n*-hexane to give colorless crystals (122 mg., 71%), m.p. 155-156.5°; ir (potassium bromide): 1766, 1720, 1685, 1671, 1650 (shoulder), 1710

Table II

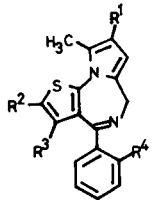
Nmr and Mass Spectral Data of 3-Benzoyl-2-(pyrrol-1-yl)thiophenes (**7**)



	Nmr (ppm, J in Hz, 100 MHz, in deuteriochloroform)	Mass [m/e (%), 70 eV]
7a	2.02 (6H, 2'-CH_3 and 4-CH_3), 2.36 (3H, s, 5-CH_3), 4.70 (2H, s, CH_2N), 5.67 and 5.98 (2H, ABq, J = 4.0 Hz, 3'-H and 4'-H), 7.20-7.90 (9H, m, C_6H_5 and C_6H_4)	454 (56, M^+), 105 (100)
7b	1.33 (3H, t, J = 7.7 Hz, CH_2CH_3), 2.05 (3H, s, 2'-CH_3), 2.87 (2H, q, J = 7.7 Hz, CH_2CH_3), 4.76 (2H, s, CH_2N), 5.85 and 6.20 (2H, ABq, J = 4.0 Hz, 3'-H and 4'-H), 6.94 (1H, s, 4-H), 7.30-8.00 (9H, m, C_6H_5 and C_6H_4)	454 (54, M^+), 105 (84), 18 (100)
7c	1.78 (3H, s, CH_3), 1.92 (3H, s, CH_3), 2.02 (3H, s, CH_3), 2.38 (3H, s, 5-CH_3), 4.75 (2H, s, CH_2N), 5.83 (1H, s, 4'-H), 7.20-7.90 (9H, m, C_6H_5 and C_6H_4)	468 (92, M^+), 105 (100)
7d	1.63 (3H, s, CH_3), 1.71 (3H, s, CH_3), 2.15 (3H, s, CH_3), 2.34 (3H, s, 5-CH_3), 4.43 (2H, s, CH_2N), 5.56 (1H, s, 4'-H), 7.00-7.30 (4H, m, CO-C_6H_4-Cl), 7.50-7.90 (4H, m, CO-C_6H_4-CO)	504 (14) and 502 (36) (M^+), 141 (37) and 139 (100)
7e	1.93 (3H, s, CH_3), 2.23 (3H, s, CH_3), 2.33 (3H, s, 5-CH_3), 4.52 (2H, s, CH_2N), 5.52 and 5.80 (2H, ABq, J = 3.2 Hz, 3'-H and 4'-H), 7.10-7.35 (4H, m, CO-C_6H_4-Cl), 7.50-7.83 (4H, m, CO-C_6H_4-CO)	490 (18) and 488 (42) (M^+), 141 (32) and 139 (100)

Table III

6-Phenyl-4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*][1.4]diazepines (8)



No.	R^1	R^2	R^3	R^4	M.p. °C (Recrystallization Solvent) (a)	Reaction Solvent Time (hours) (a)	Yield (%) (b)	Formula	*Anal.*	C (%)	H (%)	N (%)	S (%)
8a	H	CH_3	CH_3	H	154-155 (E)	E 1.5	84	$C_{19}H_{18}N_2S$	Calcd.	74.47	5.92	9.14	10.46
									Found	74.09	5.88	9.06	10.36
8b	H	C_2H_5	H	H	103.5-104 (E)	E 3.0	79	$C_{19}H_{18}N_2S$	Calcd.	74.47	5.92	9.14	10.46
									Found	74.32	6.06	8.98	10.00
8c	CH_3	CH_3	CH_3	H	173-174 (M-H)	E 1.8	65	$C_{20}H_{20}N_2S$	Calcd.	74.96	6.29	8.74	
									Found	75.06	6.30	8.63	
8d	CH_3	CH_3	CH_3	Cl	125-126 (M-H)	E-D 0.33	57	$C_{20}H_{19}ClN_2S$	Calcd.	67.69	5.40	7.89	9.03
									Found	67.88	5.36	7.64	9.24
8e	H	CH_3	CH_3	Cl	151-152 (M-H)	E-D 1.0	54	$C_{19}H_{17}ClN_2S$	Calcd.	66.95	5.03	8.22	10.40
									Found	66.66	4.95	7.94	10.95

(a) E = ethanol, M-H = methylene chloride-*n*-hexane, E-D = ethanol-*N*,*N*-dimethylformamide. (b) Yield after recrystallization.

(shoulder); nmr (deuteriochloroform): δ 2.37 (3H, s, CH_3), 4.73 (2H, s, CH_2N), 6.95 (2H, s, CH=CHCO), 7.65-7.94 (4H, m, C_6H_4).

Anal. Calcd. for $C_{14}H_{11}NO_4$: C, 65.37; H, 4.31; N, 5.45. Found: C, 65.60; H, 4.21, N, 5.63.

4-Methyl-1-phthalimidohex-3-en-2,5-dione (**3b**).

This compound was, by hydrolysis in methylene chloride with 6*N* hydrochloric acid at room temperature for 10 minutes, obtained from **2b** in 50% yield after recrystallization from methylene chloride-ethanol as colorless crystals, m.p. 116.5-117.5°; ir (potassium bromide): 1778, 1710, 1690, 1620 cm^{-1}; nmr (deuteriochloroform): δ 2.02 (3H, s, CH_3), 2.24 (3H, s, CH_3), 4.56 (2H, s, CH_2N), 6.17 (1H, s, =CHCO), 7.60-7.90 (4H, m, C_6H_4).

Anal. Calcd. for $C_{15}H_{13}NO_4$: C, 66.41; H, 4.83; N, 5.15. Found: C, 66.22; H, 4.66; N, 5.12.

1-Phthalimidohexane-2,5-dione (**5a**).

(a) Glacial acetic acid (4.5 ml.) was added to a solution of **3a** (5.65 g., 22 mmoles) in methylene chloride (70 ml.), and to the resulting solution was added under ice-cooling zinc powder (2.87 g., 44 mg.-atoms). After stirring for 75 minutes, solid was filtered off, and the filtrate was made alkaline with aqueous sodium carbonate solution. The layers were separated, and the organic layer was washed with aqueous sodium chloride solution and dried over anhydrous sodium sulfate. The solvent was evaporated, and the residue was chromatographed on silica gel (a short column) with benzene-ethyl acetate (19:1) to give colorless crystals (5.51 g., 97%). Recrystallization from methylene chloride-*n*-hexane afforded colorless crystals, m.p. 118-119.5°; ir (potassium bromide): 1770, 1722, 1610 (shoulder); nmr (deuteriochloroform): δ 2.14 (3H, s, CH_3), 2.77 (4H, s, CH_2CH_2), 4.53 (2H, s, CH_2N), 7.63-7.90 (4H, m, C_6H_4).

Anal. Calcd. for $C_{14}H_{10}NO_4$: C, 64.86; H, 5.05; N, 5.40. Found: C, 64.69; H, 4.99; N, 5.42.

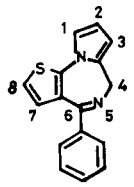
(b) Compound **3a** (614 mg., 2.39 mmoles) in ethyl acetate (30 ml.) was hydrogenated over Raney nickel (5 ml. of an ethanolic suspension prepared in the usual manner from alloy at 50° and washed throughly with water and then ethanol) at room temperature using a low pressure (ca. 1 atmosphere) hydrogenation apparatus with magnetic stirring. Uptake of the calculated amount of hydrogen required 10 minutes. The catalyst was filtered off, and the solvent was evaporated to give colorless crystals (594 mg., 96%). The ir and nmr spectra of the product were identical with those of **5a** obtained by treating **3a** with zinc-acetic acid as described above.

2-(2,5-Dioxo-*n*-hexyl)-1-hydroxy-1*H*-isoindole-3(2*H*)one (**4**).

To a solution of **3a** (175 mg., 0.68 mmole) in methylene chloride (2 ml.) was added glacial acetic acid (2 ml.) and zinc powder (0.5 g., 7.65 mg.-atoms), and the mixture was refluxed with stirring for 30 minutes. The solid was filtered off, and the filtrate was washed with water, 10% aqueous sodium carbonate solution, and aqueous sodium chloride solution and dried over anhydrous sodium sulfate. Evaporation of the solvent gave **4** as a slightly yellow oil (160 mg., 90%). Tlc on silica gel [benzene-

Table IV

Nmr and Mass Spectral Data of 6-Phenyl-4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*][1,4]benzodiazepines (**8**)



	Nmr (ppm, J in Hz, 100 MHz, in deuteriochloroform)	Mass [m/e (%), 70 eV]
8a	1.60 (3H, s, 7-CH_3), 2.30 (3H, s, CH_3), 2.42 (3H, s, CH_3), 4.00 and 5.00 (2H, ABq, J = 12.0 Hz, CH_2N), 7.10-7.80 (5H, m, C_6H_5)	306 (38, M^+), 291 (100)
8b	1.32 (3H, t, J = 8.5 Hz, CH_2CH_3), 2.47 (3H, s, 1-CH_3), 2.84 (2H, q, J = 8.5 Hz, CH_2CH_3), 4.20 and 4.98 (2H, broad s, CH_2N), 6.03 (2H, s, 2-H and 3-H), 6.56 (1H, s, 7-H), 7.22-7.80 (5H, m, C_6H_5)	306 (50, M^+), 291 (100)
8c	1.81 (3H, s, 7-CH_3), 2.01 (3H, s, 2-CH_3), 2.31 (3H, s, CH_3), 2.33 (3H, s, CH_3), 3.98 and 4.98 (2H, ABq, J = 12.0 Hz, CH_2N), 5.90 (1H, s, 3-H), 7.20-7.60 (5H, m, C_6H_5)	320 (28, M^+), 305 (100)
8d	1.52 (3H, s, 7-CH_3), 2.20 (3H, s, CH_3), 2.27 (3H, s, CH_3), 2.32 (3H, s, CH_3), 4.04 and 5.00 (2H, ABq, J = 12.4 Hz, CH_2N), 5.90 (1H, s, 3-H), 7.20-7.50 (4H, m, C_6H_4)	356 (12) and 354 (29) (M^+) 341 (41) and 339 (100)
8e	1.51 (3H, s, 7-CH_3), 2.21 (3H, s, CH_3), 2.40 (3H, s, CH_3), 4.03 and 5.07 (2H, ABq, J = 12.5 Hz, CH_2N), 5.98 (2H, s, 2-H and 3-H), 7.10-7.58 (4H, m, C_6H_4)	342 (12) and 340 (32) (M^+) 327 (39) and 325 (100)

ethyl acetate (9:1)] showed the product to be homogeneous; ir (neat): 3350, 1770 (shoulder), 1722, 1710 (shoulder); nmr (deuteriochloroform): δ 2.13 (3H, s, CH_3), 2.72 (4H, s, CH_2CH_2), 4.35 (2H, s, CH_2N), 4.1-4.6 (1H, broad, OH), 5.83 (1H, m, C*H*OH), 7.30-7.85 (4H, m, C_6H_4).

Oxidation of **4** with Chromium Trioxide.

To an ice-cold solution of **4** (160 mg., 0.61 mmole) in acetone (4 ml.) was added with stirring chromium trioxide (200 mg., 2.0 mmoles), and the mixture was stirred for 20 minutes. The mixture was diluted with methylene chloride (30 ml.), washed with water, 10% aqueous sodium carbonate solution, and aqueous sodium chloride solution, and dried over anhydrous sodium sulfate. The solvent was evaporated, and the residue was chromatographed on silica gel with benzene-ethyl acetate (17:3) to give **5a** as colorless crystals (140 mg., 88%). Recrystallization from methylene chloride-*n*-hexane afforded colorless crystals, m.p. 118-119.5°. The ir and nmr spectra of the product were identical with those of **5a** obtained by treating **3a** with zinc-acetic acid as described above.

4-Methyl-1-phthalimidohexane-2,5-dione (**5b**).

This compound was obtained by treating **3b** with zinc-acetic acid in 83% yield after recrystallization from methylene chloride-ether, m.p. 101-102°; ir (potassium bromide): 1770, 1720, 1710 cm^{-1}; nmr (deuteriochloroform): δ 1.16 (3H, d, J = 7.2 Hz, C*H*$_3$CH), 2.18 (3H, s, CH_3CO), 2.24-3.20 (3H, m, $CHCH_2CO$), ν_A 4.56 and ν_B 4.44 (2H, ABq, J = 17.4 Hz, CH_2N), 7.60-7.90 (4H, m, C_6H_4).

Anal. Calcd. for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53; N, 5.13. Found: C, 65.79; H, 5.53; N, 5.13.

3-(2-Chlorobenzoyl)-4,5-dimethyl-2-(2,3-dimethyl-5-phthalimidomethylpyrrol-1-yl)thiophene (**7d**).

A stirred solution of 2-amino-3-(2-chlorobenzoyl)-4,5-dimethylthiophene (266 mg., 1.00 mmole) and **5b** (287 mg., 1.05 mmole) in dry benzene (5 ml.) was heated at reflux with *p*-toluenesulfonic acid (20 mg.) for 10 minutes. The cooled reaction mixture was treated with saturated aqueous sodium bicarbonate solution, and the benzene layer was washed with water and then aqueous sodium chloride solution, dried over anhydrous sodium sulfate, and concentrated to give a yellow oil. The solid which resulted upon treating the oil with ether was recrystallized from methylene chloride-*n*-hexane to give **7d** (352 mg., 80% yield), m.p. 175-176°. A small sample was recrystallized from the same solvent system to give an analytical sample, colorless crystals, m.p. 175-176°; ir (potassium bromide): 1770, 1720, 1657, 1390, 1328 cm^{-1}. The nmr and mass spectral and analytical data of this compound are listed in Tables I and II.

Other 3-benzoyl-2-(pyrrol-1-yl)thiophenes (**7a-c,e**) were prepared similarly (see Tables I and II).

6-(2-Chlorophenyl)-1,2,7,8-tetramethyl-4*H*-pyrrolo[1,2-*a*]thieno[3,2-*f*][1,4]diazepine (**8d**).

A stirred solution of **7d** (350 mg., 0.70 mmole) in absolute ethanol (10 ml.) and dry *N,N*-dimethylformamide (2 ml.) was heated at reflux with hydrazine hydrate (0.3 ml.) for 20 minutes. The reaction mixture was concentrated, and benzene (25 ml.) was added. The resulting solution was washed with water and then aqueous sodium chloride solution, dried over sodium sulfate, and concentrated. Chromatography of the residual material on silica gel with ethyl acetate followed by recrystallization from methylene chloride-*n*-hexane gave **8d** (142 mg., 57% yield), m.p. 123-125°. A small sample was recrystallized from the same solvent system to give an analytical sample, colorless crystals, m.p. 125-126°; ir (potassium bromide): 1600, 1490, 1380, 1346 cm^{-1}. The nmr and mass spectral and analytical data of this compound are listed in Tables III and IV.

Other pyrrolothienodiazepines (**8a-c,e**) were prepared similarly (see Tavles III and IV).

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