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SYNTHESIS OF NOVEL CYCLIC BENZENESULFONYLUREA AND THIOUREA DERIVATIVES

Hassan M. Faidallah,[a] *Hassan A. Albar,*[b] *Mohamad S. I. Makki,*[b] *and E. M. Sharshira*[a]
Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt[a] *and Chemistry Department, Faculty of Science, University of King Abdulaziz, Saudi Arabia*[b]

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Treatment of the pyrazoline derivatives (1–6) with isocyanates or isothiocyanates afforded ureas (7–18) and thioureas (19–32) in a good yield. Subsequent treatment of the benzenesulfonylthioureas (19–32) with α- and β-halogenocarbonyl compounds gave the corresponding thiazolidines (33–41) and 1,3-thiazinones (42–46) respectively. When urea derivatives (7–18) were reacted with dimethyl malonate in sodium ethoxide, they gave the corresponding pyrazolebarbiturate derivatives (53–56). The structure of the isolated product were determined by the spectral methods.

Keywords: Pyrazolebarbiturate; thiazinone; thiazolidine; thiourea; urea

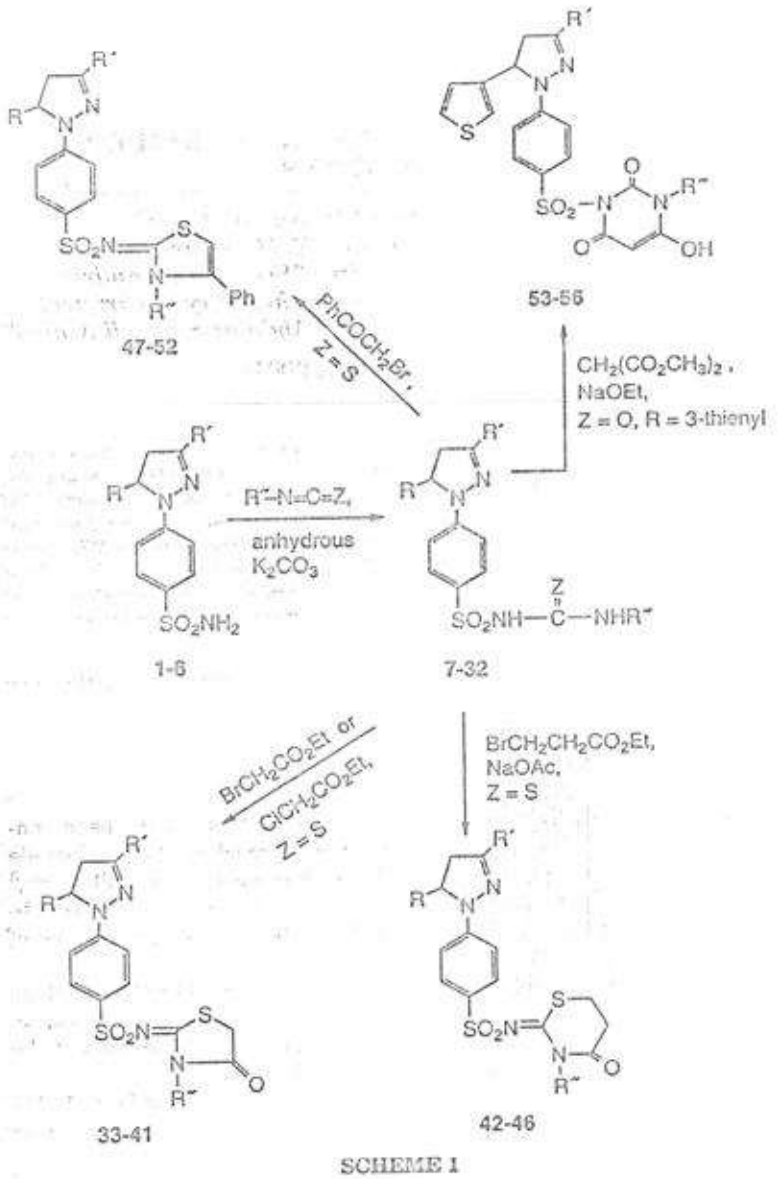
INTRODUCTION

A wide variety of pharmacological properties have been encountered with di- and trisubstituted pyrazoles. These include antiinflammatory,[1,2] antibacterial,[3,4] antineoplastic,[5] antiallergitic,[6] and hypoglycemic activites.[7–9] In this article some new di- and trisubstituted pyrazoles were prepared with the hope that they may be of potential antibacterial value.

Ureas (**7–18**) and thioureas (**19–32**) were prepared by the reactions of the pyrazolines[10] (**1–6**) with isocyanates and isothiocyanates, respectively in dry acetone under anhydrous conditions. The results of the reactions are outlined in Scheme 1 and Table I.

The IR spectra of these compounds exhibited two bands at 1334–1374 cm^{-1} and 1155–1188 cm^{-1} due to SO_2N group as well as a urea

Address correspondence to Hassan M. Faidallah, Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt.


PhCOCH2Br,
Z = S
47-52
53-56
CH2(CO2CH3)2,
NaOEt,
Z = O, R = 3-thienyl
R"-N=C=Z,
anhydrous
K2CO3
1-6
7-32
BrCH2CO2Et or
ClCH2CO2Et,
Z = S
BrCH2CH2CO2Et,
NaOAc,
Z = S
33-41
42-46

SCHEME 1

TABLE I Characteristics Data of Urea and Thiourea Derivatives

Compd. no.	R	R′	R″	X	m.p. (°C)	Mol. formula	Found (%)				Calcd. (%)			
							C	H	N	S	C	H	N	S
7	2-Furyl	Me	Cyclohexyl	O	197	$C_{21}H_{26}N_4O_4S$	58.31	6.20	12.90	7.25	58.60	6.04	13.02	7.44
8	2-Furyl	Me	Ph	O	147	$C_{21}H_{20}N_4O_4S$	59.62	4.91	12.92	7.32	59.43	4.71	13.20	7.54
9	2-Furyl	Me	Naphthyl	O	247	$C_{25}H_{22}N_4O_4S$	63.05	4.42	11.55	6.46	63.29	4.64	11.81	6.75
10	3-Thienyl	Me	Cyclohexyl	O	225	$C_{21}H_{26}N_4O_3S_2$	56.32	5.74	12.40	14.51	56.50	5.83	12.56	14.34
11	3-Thienyl	Me	Ph	O	250	$C_{21}H_{20}N_4O_3S_2$	57.06	5.62	12.66	14.70	57.27	4.54	12.72	14.54
12	3-Thienyl	Me	Naphthyl	O	230	$C_{25}H_{22}N_4O_3S_2$	61.00	4.62	11.61	12.86	61.22	4.49	11.42	13.06
13	3-Thienyl	Ph	Cyclohexyl	O	145	$C_{26}H_{28}N_4O_3S_2$	61.22	5.70	11.21	12.70	61.41	5.55	11.04	12.59
14	3-Thienyl	Ph	Ph	O	195	$C_{26}H_{22}N_4O_3S_2$	62.02	4.61	11.11	12.67	62.14	4.45	11.22	12.74
15	3-Thienyl	Ph	Naphthyl	O	225	$C_{30}H_{24}N_4O_3S_2$	64.98	4.23	9.98	11.28	65.22	4.35	10.14	11.59
16	3-Thienyl	*p*-BrC_6H_4	Cyclohexyl	O	190	$C_{26}H_{27}BrN_4O_3S_2$	53.00	4.42	9.62	11.12	53.15	4.60	9.54	10.90
17	3-Thienyl	*p*-BrC_6H_4	Ph	O	155	$C_{26}H_{21}BrN_4O_3S_2$	53.88	3.42	9.42	10.88	53.70	3.61	9.63	11.01
18	3-Thienyl	*p*-MeC_6H_4	Ph	O	200	$C_{27}H_{24}N_4O_3S_2$	62.90	4.75	11.00	12.15	62.79	4.65	10.85	12.40
19	2-Furyl	Me	Allyl	S	109	$C_{18}H_{20}N_4O_3S_2$	53.22	5.11	13.89	16.00	53.46	4.95	13.86	15.84
20	2-Furyl	Me	Benzyl	S	148	$C_{22}H_{22}N_4O_3S_2$	58.05	5.00	12.11	14.24	58.15	4.85	12.33	14.09
21	2-Furyl	Me	Ph	S	149	$C_{21}H_{20}N_4O_3S_2$	57.31	4.64	12.81	14.80	57.27	4.54	12.72	14.54
22	2-Thienyl	Me	Allyl	S	142	$C_{18}H_{20}N_4O_2S_3$	51.33	4.86	13.21	22.64	51.42	4.76	13.33	22.85
23	2-Thienyl	Me	Benzyl	S	148	$C_{22}H_{22}N_4O_2S_3$	55.98	4.38	12.01	20.32	56.17	4.68	11.91	20.42
24	2-Thienyl	Me	Ph	S	174	$C_{21}H_{20}N_4O_2S_3$	55.36	4.11	12.30	20.89	55.26	4.39	12.28	21.05
25	3-Thienyl	Me	Allyl	S	120	$C_{18}H_{20}N_4O_2S_3$	51.51	4.81	13.32	22.95	51.42	4.76	13.33	22.85
26	3-Thienyl	Me	Benzyl	S	184	$C_{22}H_{22}N_4O_2S_3$	56.00	4.81	12.03	20.35	56.17	4.68	11.91	20.42
27	3-Thienyl	Me	Ph	S	176	$C_{21}H_{20}N_4O_2S_3$	55.00	4.41	12.41	21.12	55.26	4.39	12.28	21.05
28	3-Thienyl	Ph	Benzyl	S	204	$C_{27}H_{24}N_4O_2S_3$	60.65	4.41	10.62	18.26	60.90	4.51	10.52	18.04
29	3-Thienyl	Ph	Ph	S	180	$C_{26}H_{22}N_4O_2S_3$	60.11	4.02	10.68	18.44	60.23	4.25	10.81	18.53
30	3-Thienyl	*p*-BrC_6H_4	Allyl	S	150	$C_{21}H_{21}BrN_4O_2S_3$	49.11	3.81	10.10	17.20	49.20	3.74	9.98	17.11
31	3-Thienyl	*p*-BrC_6H_4	Ph	S	186	$C_{26}H_{21}BrN_4O_2S_3$	52.31	3.32	9.18	16.00	52.26	3.52	9.38	16.08
32	3-Thienyl	*p*-$CH_3C_6H_4$	Ph	S	178	$C_{27}H_{24}N_4O_2S_3$	61.11	4.21	10.33	18.12	60.90	4.51	10.52	18.04

carbonyl band at 1647–1668 cm^{-1} in case of compounds (**7–18**) and a thiourea carbonyl absorption at 1148–1166 cm^{-1} in case of compounds (**19–32**). These data is in agreement with the suggested structures. The ^1H NMR spectra of the urea and thiourea derivatives (**7–32**), exhibited the aromatic protons as multiplets at δ 6.76–8.10 ppm region, exchangeable NH signal at δ 8.24–10.00 ppm as well as the other signals corresponds to R group (Table II).

It has been reported that condensation of N,N'-disubstituted thioureas with α-halogeno acids or esters afforded 2-imino-4-oxothiazolidines. The reaction proceeds through the intermediate formation of cyclic pseudo thiohydantoic acid.[11–13] However, in the present study cyclization of the thiourido group of the thiourea derivatives by treatment with ethyl bromoacetate (or chloroacetic acid), ethyl β-bromopropionate and α-bromoacetophenone afforded the corresponding 4-oxothiazolidines (**33–41**), 4-oxo-4,5-dihydrothiazines (**42–46**) and thiazolines (**47–52**) respectively. The results are outlined in Scheme I and Table III.

The IR spectra of thiazolidine and thiazine derivatives showed a cyclic carbonyl absorption at 1720–1742 cm^{-1} and two absorption at 1382–1372 cm^{-1} and 1165–1182 cm^{-1} for the SO_2N group. The high value of stretching vibrations for amide carbonyl of **33–41** and **42–46** would be attributed to the proximity of the imine function to the amide moiety in both cases. The structures of the above compounds were further supported by their ^1H NMR data (Table IV).

Finally, cyclization of the urea derivatives with dimethyl malonate in the presence of NaOEt afforded the corresponding pyrazolebarbiturate (pyrimidine) derivatives (**53–56**).

The IR spectra of the barbiturate derivatives showed a broad carbonyl absorption at 1671–1682 cm^{-1} as well as –OH band at 3379–3386 cm^{-1}.

EXPERIMENTAL

^1H NMR spectra were sometimes recorded on a Bruker DPX-400 FT-NMR or on a 390-90 MHz spectrometer using TMS as internal standard. IR spectra were recorded on a Nicolet FT-IR spectrometer Magna 520 and Microanalyses were performed on a 2400 Perkin Elmer Series 2 CHNS Analyser.

N'-Substituted-N^3-[*p*-(3,5-disubstituted Pyrazolin-1-yl) Benzene-sulfonyl]urea (7–18)

A mixture of the appropriate pyrazoline derivative (0.01 mol) and anhydrous K_2CO_3 (0.1 mol) in dry acetone (50 ml) was stirred and refluxed

TABLE II ^{1}H NMR Spectral Data (δ/ppm)[a] of Urea and Thiourea Derivatives

Compd. no.	R	R'	R''	X	Pyrazoline H: H-4 (2H-m)	Pyrazoline H: H-5 (1H, m)	ArH + NH (m)		CH_3	Other
7	2-Furyl	Me	Cyclohexyl	O	2.85–3.45	5.10–5.39	6.99–7.80	(7H)	2.18	1.44 (11H, m, cyclohexyl)
8	2-Furyl	Me	C_6H_5	O	2.82–3.58	5.35–5.58	7.00–7.95	(12H)	2.18	6.25 (2H, H3', 4' of furan, m)
9	2-Furyl	Me	Naphthyl	O	2.80–3.68	5.45–5.40	6.98–8.00	(14H)	2.19	6.35 (2H, H3', 4' of furan, m)
10	3-Thienyl	Me	Cyclohexyl	O	2.88–3.65	5.30–5.52	6.84–7.70	(9H)	2.12	6.20 (2H, H3', 4' of furan, m)
11	3-Thienyl	Me	C_6H_5	O	2.82–3.68	5.22–5.48	6.76–7.72	(13H)	2.18	1.42 (11H, m, cyclohexyl)
12	3-Thienyl	Me	Naphthyl	O	2.80–3.72	5.24–5.50	6.82–8.05	(15H)	2.10	8.28 (1H, S_b, NH)
16	3-Thienyl	p-BrC_6H_5	Cyclohexyl	O	2.85–3.90	5.35–5.76	6.85–8.00	(13H)		1.45 (m, 11H, cyclohexyl)
20	2-Furyl	CH_3	Benzyl	S	2.85–3.65	5.15–5.45	7.00–7.70	(12H)	2.24	4.80 (2H, d, J = 6 Hz, CH_2); 6.30 (2H, H3', 4' of furan, m); 8.40 (1H, S_b, NH)
21	2-Furyl	Me	C_6H_5	S	2.90–3.65	5.16–5.48	7.00–7.98	(12H)		9.80 (1H, S_b, NH); 6.30 (2H, H3', 4' of furan);
23	2-Thienyl	Me	Benzyl	S	2.75–3.70	5.38–5.72	6.85–8.00	(13H)	2.24	4.82 (2H, d, J = 6 Hz, CH_2); 8.70 (1H, t, NH)
26	3-Thienyl	Me	Benzyl	S	2.65–3.64	5.20–5.52	6.45–7.90	(13H)	2.20	4.78 (2H, d, J = 6 Hz); 8.70 (1H, t, NH)
28	3-Thienyl	C_6H_5	Benzyl	S	3.00–4.22	5.70–5.99	6.95–8.10	(18H)		4.80 (2H, d, J = 6 Hz, CH_2); 8.94 (1H, t, NH)
29	3-Thienyl	C_6H_5	C_6H_5	S	3.20–4.08	5.35–5.68	6.92–7.94	(18H)		

[a] Solutions in a mixture of $CDCl_3$ and DMSO-d_6.

TABLE III Characteristics Data of Thiazolidine, Thiazine, Thiazoline, and Pyrimidine Derivatives

Compd. no.	R	R'	R''	m.p. (°C)	Mol. formula	Found (%)				Calcd. (%)			
						C	H	N	S	C	H	N	S
33	2-Furyl	Me	Allyl	150	$C_{26}H_{20}N_4O_4S_2$	54.11	4.62	12.34	14.20	54.05	4.50	12.61	14.14
34	2-Furyl	Me	Benzyl	126	$C_{24}H_{22}N_4O_4S_2$	58.40	4.56	11.36	13.11	58.29	4.45	11.33	12.95
35	2-Furyl	Me	Ph	238	$C_{23}H_{20}N_4O_4S_2$	57.64	4.26	11.89	13.15	57.50	4.17	11.66	13.33
36	2-Thienyl	Me	Allyl	135	$C_{20}H_{20}N_4O_3S_3$	52.37	4.67	12.38	21.00	52.17	4.34	12.17	20.86
37	2-Thienyl	Me	Benzyl	176	$C_{24}H_{22}N_4O_3S_3$	56.58	4.28	11.11	18.55	56.47	4.31	10.98	18.82
38	2-Thienyl	Me	Ph	250	$C_{23}H_{20}N_4O_3S_3$	55.78	4.09	11.38	19.26	55.64	4.03	11.29	19.35
39	3-Thienyl	Me	Benzyl	124	$C_{24}H_{22}N_4O_3S_3$	56.66	4.37	11.21	18.76	56.47	4.31	10.98	18.82
40	3-Thienyl	Me	Ph	242	$C_{23}H_{20}N_4O_3S_3$	55.81	3.87	11.42	19.20	55.64	4.03	11.29	19.35
41	3-Thienyl	Ph	Ph	−272	$C_{28}H_{22}N_4O_3S_3$	60.33	3.81	10.03	17.05	60.21	3.94	10.03	17.20
42	2-Furyl	Me	Ph	230	$C_{24}H_{22}N_4O_4S_2$	58.49	4.48	11.63	13.00	58.29	4.45	11.33	12.95
43	2-Thienyl	Me	Ph	204	$C_{24}H_{22}N_4O_3S_3$	56.30	4.22	11.02	18.66	56.47	4.31	10.98	18.82
44	3-Thienyl	Me	Ph	248	$C_{24}H_{22}N_4O_3S_3$	56.62	4.05	11.12	18.78	56.47	4.31	10.98	18.82
45	3-Thienyl	Ph	Ph	240	$C_{24}H_{24}N_4O_3S_3$	61.01	4.20	10.00	16.94	60.83	4.19	9.79	16.78
46	3-Thienyl	p-$CH_3C_6H_4$	Ph	232	$C_{30}H_{26}N_4O_3S_3$	61.32	4.22	9.31	16.63	61.43	4.43	9.56	16.38
47	2-Furyl	Me	Ph	184	$C_{29}H_{24}N_4O_3S_2$	64.30	4.22	10.12	12.12	64.30	4.44	10.37	11.85
48	2-Thienyl	Me	Benzyl	155	$C_{30}H_{26}N_4O_2S_3$	64.31	4.77	10.11	16.91	64.74	4.67	10.07	16.84
49	2-Thienyl	Me	Ph	188	$C_{29}H_{24}N_4O_2S_3$	62.49	4.25	9.51	17.08	62.59	4.32	10.07	17.27
50	3-Thienyl	Me	Ph	168	$C_{29}H_{24}N_4O_2S_3$	62.68	4.31	10.01	17.15	62.59	4.32	10.07	17.27
51	3-Thienyl	Ph	Benzyl	218	$C_{35}H_{28}N_4O_2S_3$	66.41	4.39	15.21	15.41	66.45	4.43	15.19	15.18
52	3-Thienyl	Ph	Ph	174	$C_{34}H_{26}N_4O_2S_3$	66.21	4.05	9.11	15.72	66.02	4.21	9.06	15.53
53	3-Thienyl	Me	Ph	130	$C_{24}H_{20}N_4O_5S_2$	57.00	3.72	11.11	12.38	56.69	3.94	11.02	12.60
54	3-Thienyl	Ph	cyclohexyl	196	$C_{29}H_{28}N_4O_5S_2$	60.25	4.92	9.57	10.89	60.41	4.86	9.72	11.11
55	3-Thienyl	p-BrC_6H_4	cyclohexyl	224	$C_{29}H_{27}BrN_4O_5S_2$	53.05	4.00	8.32	10.01	53.13	4.12	8.55	9.77
56	3-Thienyl	p-BrC_6H_4	Ph	158	$C_{29}H_{21}BrN_4O_5S_2$	53.39	3.12	8.41	9.66	53.62	3.23	8.63	9.56

TABLE IV ^{1}H NMR Spectral Data (δ/ppm)[a] of Thiazolidine, Thiazine, Thiazoline, and Pyrimidine Derivatives

Compd. no.	R	R′	R″	Pyrazoline H: H-4 (2H-m)	Pyrazoline H: H-5 (1H, m)	ArH (m)		CH_3	Thiazolidine H (2H, s)	Other
33	2-Furyl	Me	Allyl	2.88–3.75	5.52–5.85	7.02–7.85	(5H)	2.19	4.02	6.38 (2H, m, H3′, 4′ of furan)
35	2-Furyl	Me	Ph	2.95–3.85	5.40–5.65	7.00–8.00	(10H)	2.18	4.30	1.45 (2H, m, H3′, 4′ of furan)
37	2-Thienyl	Me	Benzyl	2.70–3.98	5.50–5.78	6.98–8.00	(12H)	2.15	4.10	4.84 (2H, s, CH_2 of benzyl)
38	2-Thienyl	Me	Ph	2.80–3.95	5.52–5.80	6.88–7.86	(12H)	2.16	4.15	
41	2-Thienyl	Ph	Ph	3.22–4.15	5.20–6.12	6.98–7.80	(17H)		4.20	
42	2-Furyl	Me	Ph	2.50–3.70[b]	5.38–5.60	6.95–7.92	(10H)	2.19		6.40 (2H, m, H3′, 4′ of furan)
45	3-Thienyl	Ph	Ph	3.15–4.22[b]	5.80–6.20	6.78–7.95	(17H)			
47	2-Furyl	Me	Ph	2.80–3.78	5.28–5.50	2.00–8.00	(16H)	2.16		6.38 (2H, m, H3′, 4′ of furan)
49	2-Thienyl	Me	Ph	2.98–4.05	5.42–5.68	6.90–7.96	(18H)	2.30		
52	3-Thienyl	Ph	Ph	3.00–4.22	5.40–5.72	6.82–7.80	(23H)			
53	3-Thienyl	Me	Ph	2.89–3.98	5.32–5.60	6.88–7.96	(14H)[c]	2.25		
54	3-Thienyl	Ph	cyclohexyl	3.34–4.38	5.52–5.80	6.98–8.00	(14H)[c]			0.075–1.4 (11H, m, cyclohexyl H)

[a] Solutions in a mixture of $CDCl_3$ and DMSO-d_6.
[b] 6H (H-4 + $2CH_2$ of thiazine).
[c] ArH + OH.

1 h. At this temperature a solution of the proper isocyanate (0.01 mol) in dry acetone (5 ml) was added in a dropwise manner. After the mixture was stirred and refluxed for 18 h in nitrogen atomosphere, acetone was removed under reduced pressure, and the solid residue was dissolved in water. The crude product was isolated by acidification with 2*M* HCl and purified by recrystallisation from ethanol as needles.

N′-Substituted-N³-[*p*-(3,5-disubstituted Pyrazolin-1-yl) Benzene-sulfonyl]thiourea (19–32)

A mixture of the appropriate pyrazoline derivative (0.01 mol) and anhydrous K_2CO_3 (0.1 mol) in dry acetone (50 ml) was stirred and refluxed 1 h. At this temperature a solution of the proper isothiocyanate (0.01 mol) in dry acetone (5 ml) was added in a dropwise manner. After the mixture was stirred and refluxed for 10 h in nitrogen atmosphere, acetone was removed under reduced pressure, and the solid resiue was dissolved in water. The crude product was isolated by acidification with 2*M* HCl and purified by recrystallisation from ethanol as needles.

3-Substituted-2-[*p*-(3,5-disubstituted Pyrazolin-1-yl) Benzene-sulfonyl]-4-oxothiazolidines (33–41)

A solution of the appropriate thiourea derivative (0.002 mol) in absolute ethanol (10 ml) was refluxed with ethylbromoacetate or chloroacetic acid (0.002 mol) and NaOAc (0.005 mol, 2 ml H_2O) for 2 h. The reaction mixture was then cooled and poured into ice-cold water; the product that separated was recrystallized from ethanol-benzene mixture as needles.

3-Substituted-2-[*p*-(3,5-disubstituted Pyrazolin-1-yl) Benzene-sulfonyl]-4-oxo-5,6-dihydro-1,3-thiazines (42–46)

A solution of the appropriate thiourea derivative (0.002 mol) in absolute ethanol (10 ml) was refluxed with ethyl β-bromopropionate (0.002 mol) and NaOAc (0.005 mol, 2ml H_2O) for 2 h. The reaction mixture was then cooled, filtered, washed with water, and recrystallized from ethanol as needles.

3-Substituted 2-[*p*-(3,5-disubstituted Pyrazolin-1-yl) Benzene-sulfonyl]-4-Phenylthiazolidines (47–52)

A solution of the appropriate thiourea derivative (0.002 mol) in absolute ethanol (10 ml) was refluxed with α-bromoacetophenone (0.002 mol) for 2 h. The product that separated during heating was allowed to cool, filtered, and recrystallized from ethanol as needles.

3-Substituted-1-[*p*-(3-thienyl-5-phenylpyrazol-1-yl) Benzene-sulfonyl]-4-hydroxy-2,6-dioxopyrimidines (53–56)

To a solution of sodium ethoxide in ethanol (0.023 g Na, 8 ml ethanol) was added successively, diethylmalonate (0.001 mol) and the appropriate urea derivative (0.001 mol) in hot ethanol (10 ml). The resulting mixture was heated on water bath at 100°C for 2 h. The sodium salt which precipitated during heating was filtered, dissolved in water (20 ml), and acidified with conc. HCl. The solid which separated was collected, washed with water, and recrystallized from ethanol as needles.

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