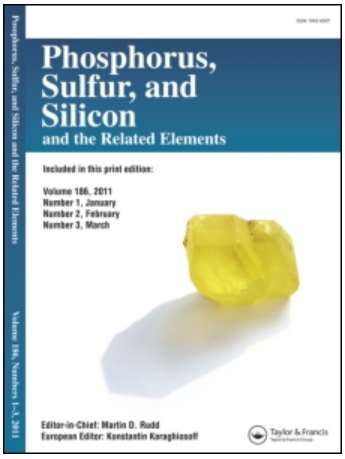

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SYNTHESIS OF THIENO(2,3-b)THIOPHENES AND RELATED STRUCTURES

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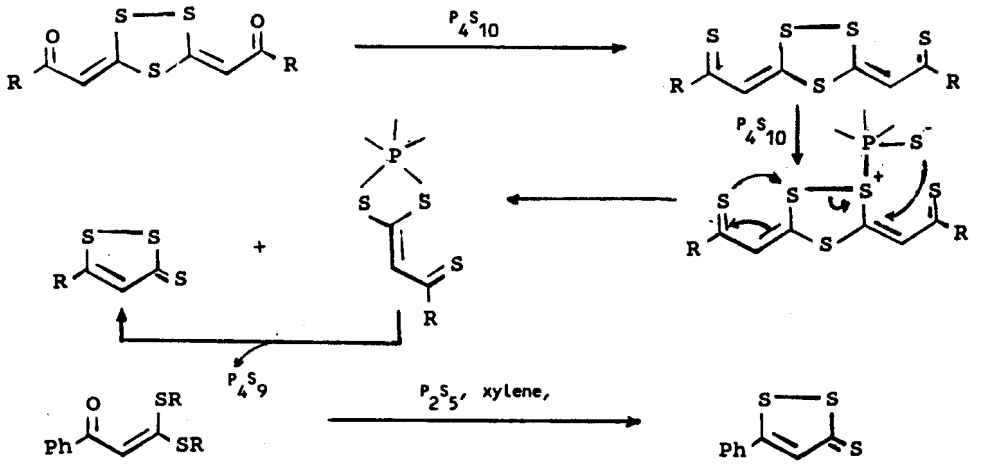
Some new functionally substituted thieno(2,3-b)thiophenes and related compounds were obtained in a one-pot reaction using phase transfer catalysis conditions starting with some active nitriles or active methylene compounds, carbon disulphide or phenyl isothiocyanate and α-chlorocarbethoxy, or α-nitrile electrophiles. The structure of the obtained new compounds was assigned.

Key words: Thiophene; thienothiophene; dithiolane; thiazolidinone; thiazoline; thienopyrazole; furopyrazole.

INTRODUCTION

Two general strategies have been developed for the synthesis of thiophenes from conjugated S,S- and N,S-acetals. The first involves the synthesis of conjugated ketene dithioacetal containing an S-alkyl group (e.g., CH_3, CH_2CN, CH_2COR, CH_2COOR) that can undergo subsequent cyclization onto the conjugated functionality (e.g., CN, COR, COOR). The second strategy involves cyclization of the enamine moiety of ketene N,S-acetals onto an S-alkyl unit (e.g., $CH_2C{\equiv}C$, $CH{=}C{=}CH_2$).[1]



Thiophene formation was observed during studies on the alkylation of dithioic acids or the monoanions derived from them. Gompper and Schafer[2] reported that alkylation of the dithioic acid derived from methyl cyanoacetate with α-chloroac-

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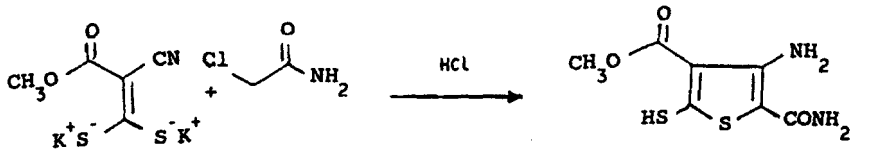
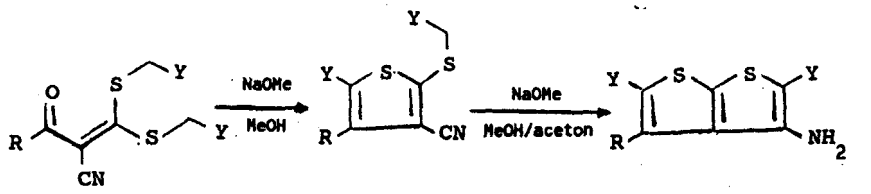
etamide under acidic conditions yielded a thiophene arising from S-alkylation followed by closure onto the nitrile. A similar procedure involving the S-alkylation of dithioic acid anions with α-chloroketones was observed to afford thiophenes.[3] The dithioic acid anion, however, was derived from acetylacetone and a mixture of thiophenes and thienothiophenes products were obtained in modest yields.



Alkylation of dithioic dianions derived from α-cyanoketones[4] with α-haloesters, nitriles and ketones has been examined as a general route to thiophenes. The dithiolate dianions can be sequentially alkylated with CH_3I and XCH_2Y(Y = CN, COR, COOR) to afford mixed ketene dithioacetals or treated with two equivalents of the α-halocarbonyl or nitrile electrophile. The latter compound can be converted in two steps into thienothiophenes.



The introduction of phase transfer catalysis in carbanionic reactions offers one of the most important recent methods of organic synthesis. It is important because it simplifies procedures, eliminates expensive, inconvenient and dangerous reactants and solvents, and also allows one to perform many reactions that otherwise proceed in an unsatisfactory way or do not proceed at all. PTC have been reviewed[5–17] but only two reviews deal with the chemistry of heterocyclic compounds.[18,19] Most PTC reactions take place in liquid-liquid two phase systems in which both phases, aqueous alkali and organic reactants (neat or in a non polar solvent) are mutually immiscible. Despite many advantages, this system has some limitations, one of them being the hydrolytic activity of concentrated aqueous alkali. However, solid-liquid two phase systems offers a convenient alternative. Reactions are catalyzed by tetrabutylammonium bromide or a crown ether. In solid-liquid PTC systems the catalysts are unable to transfer carbonate anions (CO_3^{-2}) into the organic phase[20] thus solid-liquid phase transfer phenomena are not involved here.

RESULTS AND DISCUSSION

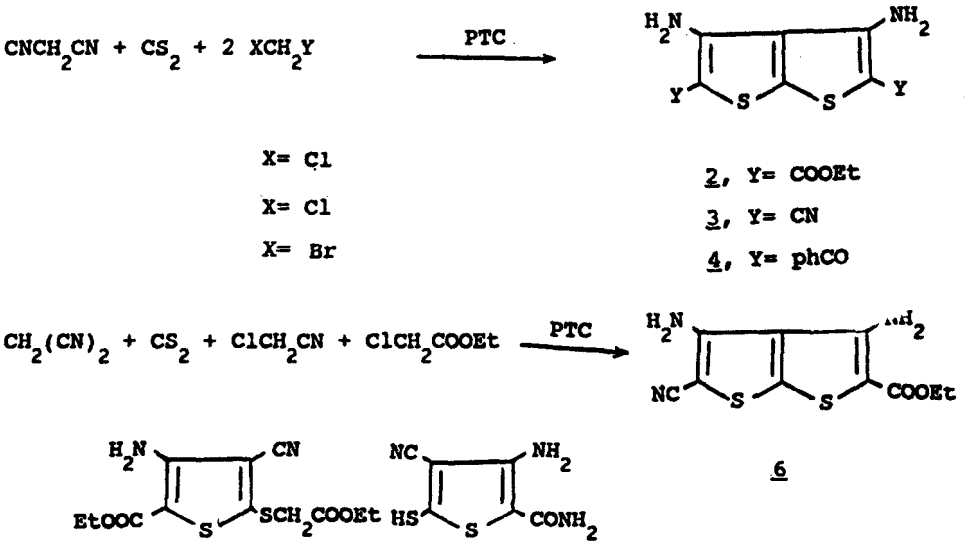
In connection with our work on PTC reactions,[21–25] we report here the synthesis of some new functionally substituted thieno(2,3-b)thiophenes in a one-pot reaction by using PTC conditions [K_2CO_3/benzene/tetrabutylammonium bromide (TBAB catalyst] starting with some active nitriles, CS_2 and α-chlorocarbethoxy, or α-nitrile electrophiles in 1:1:2 molar ratios.

The reaction of malononitrile, CS_2 with ethylchloroacetate, chloroacetonitrile or phenacyl bromide was carried out under PTC conditions by stirring the reactants at different temperatures over different periods of time (Table I) where the corresponding thieno(2,3-b)thiophenes (2–4) were obtained in excellent yields. During the course of reaction with ethyl chloroacetate the intermediate thiophene derivative 1 was isolated by reducing the time of the reaction (cf. Table I). This is in accordance with the stepwise nature of this type of reaction. This behaviour was also substantiated by carrying out a one-pot reaction starting with $CH_2(CN)_2$, CS_2, $ClCH_2CN$ and $ClCH_2COOEt$ in 1:1:1:1 molar ratio where 3,4-diamino-2-carbethoxy-5-cyanothiophene 6 was obtained as the end product. The reaction of malononitrile, CS_2 and chloroacetamide was carried out in 1:1:1 molar ratio where 3-amino-2-carboxyamido-4-cyano-5-mercaptothiophene 5 was obtained.

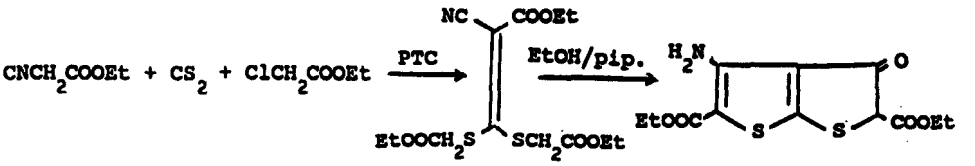
In analogy with malononitrile, the reaction of ethyl cyanoacetate, CS_2 along with two moles of ethyl chloroacetate afforded 2-carbethoxy-2,3-dicarbethoxymethyl-mercapto-acrylonitrile 7 rather than the expected compound 3-amino-2,5-dicarbethoxy-5-hydro-thieno(2,3-b) thiophene 8 which was easily obtained from 7 by boiling in ethanol in the presence of piperidine catalyst for about 30 minutes. The reaction of ethyl cyanoacetate along with CS_2 and bromomalononitrile in 1:1:1 molar ratio was also attempted under the applied PTC conditions where the 1,3-dithiolane derivative, namely, 5-cyano-4-imino-1,3-dithiolane-2-ylidene-ethyl cyanoacetate 9 was obtained *via* HBr elimination followed by a nucleophilic attack of mercapto group onto the cyano function (Scheme 2).

Ethyl acetoacetate, CS_2 and $ClCH_2CN$ in 1:1:2 molar ratio were also reacted under the applied PTC conditions where a mixture of the corresponding thiophene 10 and thienothiophene 11 derivatives were obtained (Scheme 3).

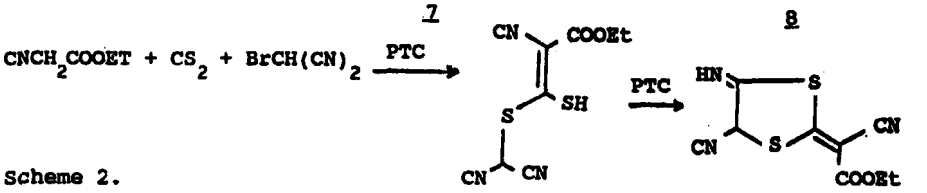
We reported here also a general route to thiazolidines by reacting a mixture of malononitrile, phenyl isothiocyanate and ethyl chloroacetate in 1:1:2 molar ratio. After 5 hours of stirring at 60°C a mixture of the disubstituted ketene-N,S-acetal



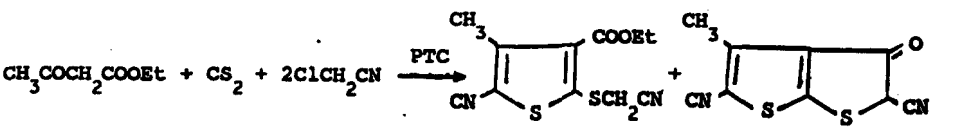
Scheme 1. 1 5



7 8



Scheme 2. 9

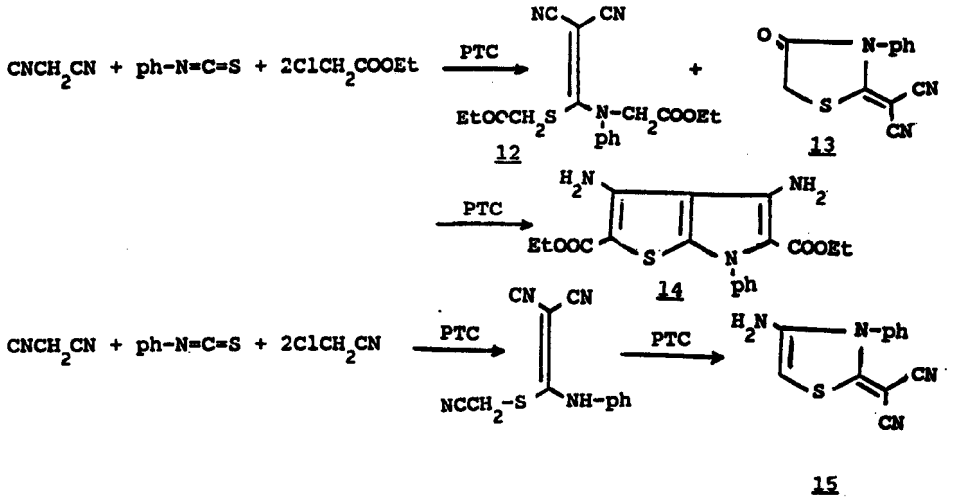


10 11

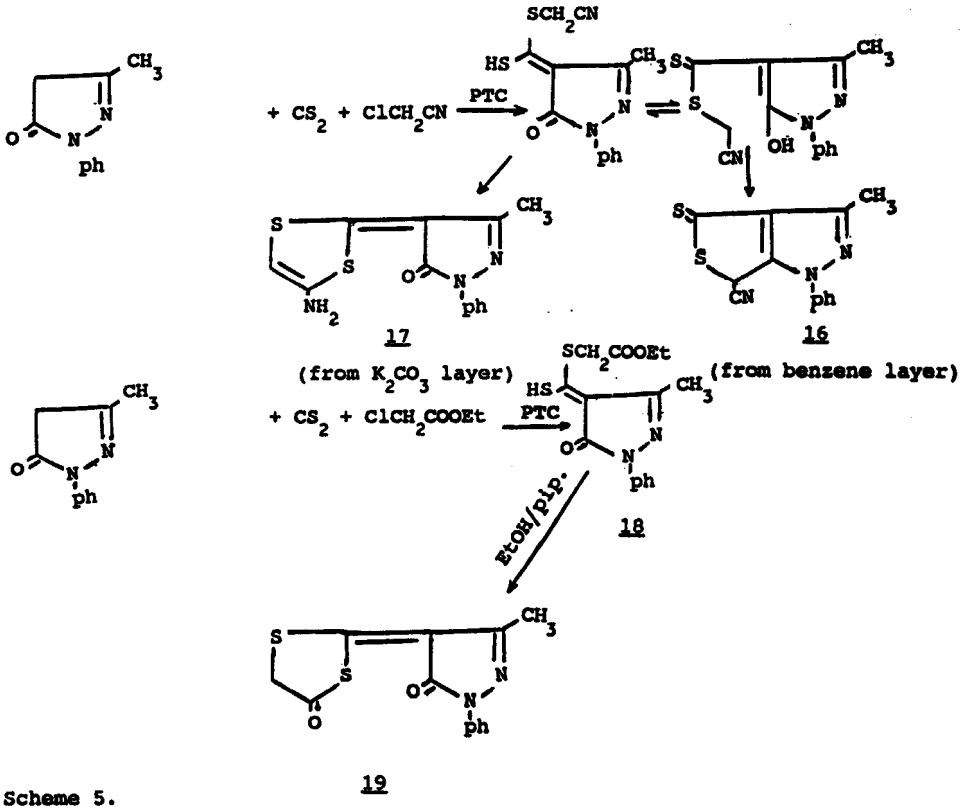
Scheme 3.

12 along with the thiazolidinone derivative 13, were obtained. Compound 13 was derived from the S-substituted ketene-N,S-acetal by a nucleophilic attack of the NH group at the carbonyl function with loss of ethanol molecule, this result is in favour of the stated higher reactivity of S compared to the N anionic pole. Under the applied conditions compound 12 was not cyclized into the desired thienopyrrole derivative 14, however after 5 more hours at 60°C in a new catalytic two-phase PTC system it was obtained in an excellent yield. When $ClCH_2CN$ was substituted for $ClCH_2COOEt$ in the former reaction we were able to obtain directly the 4-amino-2-cyanomethylene-3-phenyl thiazoline 15 which is due to the formation of the S-substituted ketene N,S-acetal followed by a rapid nucleophilic attack of NH (and not the CH group) at the cyano function. This is again in accordance with the sequence of reactivity of anionic poles S > N ≃ C > O (Scheme 4).

Heterocyclic systems containing active methylene group were also successfully reacted under PTC conditions, thus 3-methyl-1-phenyl-pyrazol-5-one when reacted with CS_2 and $ClCH_2CN$ in 1:1:1 ratio the reaction afforded two products, 6-cyano-4,6-dihydro-3-methyl-1-phenyl-thieno(3,4-c)pyrazol-4-thione 16 which was obtained from benzene layer and 3-methyl-*N*-phenyl-4-[4-amino-1,3-dithiolane-4-ene-2-ylidene]-pyrazol-2-ene-5-one 17 which was precipitated during the reaction. The reaction mechanism was assumed to involve an addition of active CH_2 group at CS_2 to give the intermediate product which was cyclized either by a nucleophilic attack of CNCH:—atom onto the tautomeric C—OH moiety to give compound 16 or by a direct addition of SH group onto the cyano function to give compound 17 (Scheme 5).



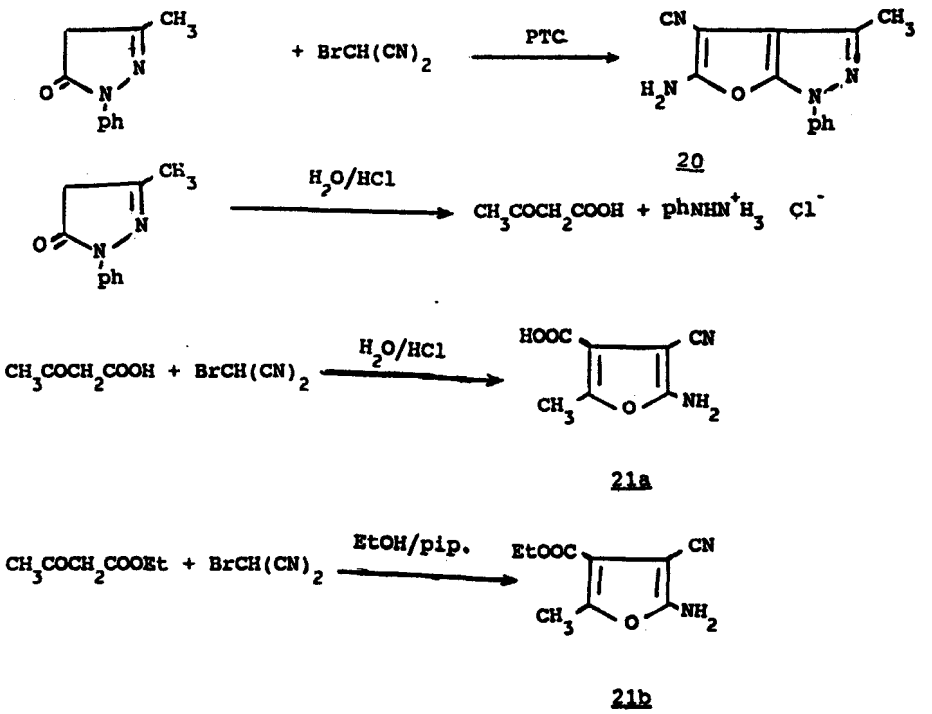
Scheme 4.



Scheme 5.

Substitution of $ClCH_2CN$ with $ClCH_2COOEt$ in the former reaction gave a simple substitution product, 3-methyl-*N*-phenyl-4-[(carbethoxymethylmercapto)mercaptoethylene]pyrazol-2-ene-5-one 18 which was only cyclized in boiling ethanol into 3-methyl-*N*-phenyl-4-(5-oxo-1,3-dithiolane-2-ylidene)-pyrazol-2-ene-5-one 19 *via* nucleophilic addition of SH group onto the carbonyl ester with elimination of ethanol molecule (Scheme 5).

The reaction of pyrazolone with bromomalononitrile in 1:1 molar ratio under PTC condition was also carried out. At the end of the reaction 5-amino-4-cyano-3-methyl-*N*-phenyl furo(2,3-c)pyrazole 20 was separated from benzene layer, however, its yield was low (38%) compared with the average yields obtained during this study. The aqueous layer obtained by dissolving solid potassium carbonate in water was neutralized with dil. HCl and was left for 3 days at room temperature where a solid product was precipitated and was proved to be 2-amino-4-carboxy-3-cyano-5-methyl furan 21a. The mechanism of formation of compound 20 was assumed to involve HBr elimination followed by a nucleophilic attack of the OH group at the cyano function and cyclization. The formation of 21a was due to the hydrolytic cleavage of unreacted pyrazolone into acetoacetic acid and phenylhydrazine. This acid was attack *in situ* with unreacted bromomalononitrile to give 21a. This conclusion was proved by reacting acetoacetic ester with bromomalononitrile in boiling ethanol containing a few drops of piperidine for 15 minutes where 2-amino-4-carbethoxy-3-cyano-5-methyl furan 21b was obtained (Scheme 6).



Scheme 6.

EXPERIMENTAL

Phase Transfer Catalysis Technique—General Procedure: 0.05 Mole of the active methylene compounds, e.g., malononitrile, ethyl cyanoacetate, ethyl acetoacetate, along with 0.05 mole of CS_2 or 0.05 mole of phenylisothiocyanate in 70 ml of benzene was treated with 3 grams of anhydrous potassium carbonate. The formed dianionic ambident compound was then treated with 0.05 mole or 0.1 mole of the reactive halo derivative including chloroacetonitrile, ethyl chloroacetate, phenacyl bromide, chloroacetamide or bromomalononitrile and a catalytic amount of the tetrabutyl ammonium bromide (TBABr, 3 mmole). The reaction mixture was stirred over periods of time and at different temperatures (Table I), whereby a noticeable change in colour was observed.

At the end of the reaction, TLC, the organic layer was separated, washed thoroughly with water, dried over anhydrous magnesium sulphate and evaporated *in vacuo*. The residue was washed with light petroleum ether and collected by filtration.

TABLE I

Compound	T (°C)	t (h)	Yield (%)	M.P[a] Cryst.Solv.	Mol.Form.[b] Mol.Wt.
1	60	4	80	140-2 (Benzene)	$C_{12}H_{14}N_2O_4S_2$ (314.4)
2	60	6	88	201-2 (Ethanol)	$C_{12}H_{14}N_2O_4S_2$ (314.4)
3	25	1	81	210[d] (Ethanol)	$C_8H_4N_4S_2$ (220.3)
4	60	6	55	165 (Ethanol)	$C_{20}H_{14}N_2O_2S_2$ (378.45)
5	60	8	73	170-1 (Methanol)	$C_6H_5N_3OS_2$ (199.2)
6	60	4	88	225-6 (Benzene)	$C_{10}H_9N_3O_2S_2$ (267.3)
7	60	4	76	215-6 (Ethanol)	$C_{14}H_{19}NO_6S_2$ (361.4)
8			63	275-6 (Ethanol)	$C_{12}H_{13}NO_5S_2$ (315.4)
9	60	3	58	245-8 (Methanol)	$C_9H_7N_3O_2S_2$ (253.3)
10	60	3	47	124.5 (Benzene)	$C_{11}H_{10}N_2O_2S_2$ (266.3)
11	25	4	32	>300 (Ethanol)	$C_9H_4N_2OS_2$ (220.3)
12	60	8	62	175-6 (Ethanol)	$C_{18}H_{19}N_3O_4S$ (373.4)
13	60	8	12	275-6 (Benzene)	$C_{12}H_7N_3OS$ (241.3)
14			72	>300 (Benzene)	$C_{18}H_{19}N_3O_4S$ (373.4)
15	25	4	65	140-1 (Ethanol)	$C_{12}H_8N_4S$ (240.3)
16	25	3	28	125 (Benzene)	$C_{13}H_9N_3S_2$ (271.35)

TABLE I (*Continued*)

17	25	3	42	180 (Ethanol)	$C_{13}H_{11}N_3OS_2$ (289.4)
18	40	3	74	115-6 (Ethanol)	$C_{15}H_{16}N_2O_3S_2$ (336.4)
19			88	175-6 (Ethanol)	$C_{13}H_{10}N_2O_2S_2$ (290.35)
20	40	3	38	215-7 (Ethanol)	$C_{13}H_{10}N_4O$ (238.24)
21_a	40	3	28	177-8 (H_2O)	$C_7H_6N_2O_3$ (166.13)
21_b			76	208-10 (Ethanol)	$C_9H_{10}N_2O_3$ (194.2)

TABLE II

Comp.	IR (KBr) [c] Cm	^{1}H-nmr (DMSO-d_6) [d] , (ppm)
1	3450,3350(NH_2), 2200(CN), 1730,1720(C=O ester).	6.10(br,2H,NH_2), 4.40-4.10 (m,4H,$2CH_2$ ester), 3.80 (s,2H,CH_2), 1.40-1.10(m,6H, $2CH_3$ ester) DMSO.
2	3450,3350(NH_2), 2980-2950 (C-H) alif., 1730(C=O ester).	7.30(br,4H,NH_2), 4.60-4.10 (q,4H,$2CH_2$), 1.50-1.10(t,6H, $2CH_3$) DMSO.
3	3370,3260(NH_2), 2210(CN).	5.30(br,4H,$2NH_2$) DMSO.
4	3420,3310(NH_2), 3030(C-H, arom.), 1710(C=O), 780, 710(C-H phenyl).	7.70-7.30(m,10H,arom), 5.40 (br,4H,$2NH_2$) $CDCl_3$.
5	3420,3300,3190(NH_2), 2200 (CN), 1690(C=O).	3.60(br,1H,SH), 7.30(br,2H, NH_2), 4.70(br,2H,$CONH_2$)DMSO
6	3420,3300,3180(NH_2),2950 (C-H), 2200(CN), 1720 (C=O ester).	7.20(br,2H,NH_2 in position 3 6.50(br,2H,NH_2 in position 4 4.40-4.00(q,2H,CH_2), 1.40-1.10(t,3H,CH_3) DMSO.
7	2980,2970(C-H), 2200 (CN),1720,1715(C=O ester), 1610(C=C) .	4.30-3.90(m,6H,$3CH_2$ ester), 3.60(s,4H,$2CH_2$), 1.30-1.10(m, 9H,$3CH_3$) DMSO.
8	3430,3340(NH_2), 2980, 2920(C-H), 1730,1720 (C=O ester), 1670(C=O)	6.70(s,2H,NH_2), 4.30-3.90(q, 4H,$2CH_2$), 3.80(s,1H,CH-carbe-thoxy), 1.30-1.00(t,6H,$2CH_3$) DMSO .

TABLE II (*Continued*)

9	3350(NH), 2980,2920 (C-H), 2200(CN), 1750 (C=O ester), 1620(C=C).	9.10-8.90(br,1H,NH), 4.30-3.90(q,2H,CH_2), 3.80(s,1H, CH-N), 1.30-1.00(t,3H,CH_3) DMSO .
10	2980(C-H), 2210,2200(CN) ,1730(C=O ester), 1620 (C=O).	4.40-4.10(q,2H,CH_2 ester) 4.05(s,2H,CH_2CN), 2.80(s,3H, CH_3), 1.75-1.40(t,3H,CH_3) DMSO
11	2980(C-H), 2215,2210(CN) , 1670(C=O), 1620(C=C).	4.20(br,1H,CH-CN), 2.80(s,3H, CH_3) DMSO.
12	3030(C-H), 2970(C-H), 2220(CN),1720(C=O ester)	8.20-7.80(m,5H,arom), 4.50-3.90(m,8H,2CH_2+2CH_2ester), 1.60-1.10(m,6H,2CH_3 ester) $CDCl_3$.
13	3030(C-H), 2970(C-H), 2210,2200(CN),1670(C=O) ,780,710(C-H phenyl).	7.55-7.40(m,5H,arom.), 4.40 (s,2H,CH_2) DMSO.
14	3420,3360,3240(NH_2), 3030(C-H), 2970(C-H), 1730,1715(C=O ester), 780,710(C-H phenyl).	7.45-7.30(m,5H,arom), 6.20 (br,4H,2NH_2), 4.40-4.15(qq, 4H,2CH_2 ester), 1.30-1.10 (tt,6H,2CH_3) DMSO .
15	3320,3210(NH_2), 3050 (C-H arom.), 2210,2200 (CN), 1620(C=C)	7.70-7.60(m,5H,arom), 7.50 (s,1H,=CH), 5.70(s,2H,NH_2) DMSO.
16	3030(C-H), 2980(C-H), 2200(CN), 1670(C=N), 1130(C=S), 780,710(CH, phenyl)	7.90-7.30(m,5H,arom), 5.40(s, 1H,CH-CN), 2.10(s,3H,CH_3) DMSO.
17	3420,3330(NH_2), 3050(C-H) , 2980(C-H),1680(C=O), 1670(C=N).	8.20-7.90(m,2H arom), 7.60-7.20(m,3H,arom), 6.10(br,1H, =CH), 5.40(br,2H,NH_2), 2.30 (s,3H,CH_3) DMSO.
18	3030(C-H), 2950,2900(C-H) , 1710(C=O ester), 1680 (C=O), 1670(C=N), 780,710 (C-H phenyl).	8.20-8.00(m,2H,arom), 7.40-7.10(m,3H,arom), 4.30-4.00 (m,4H,CH_2+CH_2 ester), 3.10 (s,1H,SH), 2.65(s,3H,CH_3), 1.40-1.10(t,3H,CH_3) DMSO.
19	3030(C-H), 2950,2900(C-H) 1680(C=O), 1670(C=O), 1660(C=N), 780,710(C-H phenyl).	7.90-7.40(m,5H,arom), 4.20 (s,2H,CH_2), 2.70(s,3H,CH_3) DMSO .

TABLE II (*Continued*)

20	3410,3300(NH_2), 3030(C-H), 2980(C-H), 2200(CN) 1670(C=N).	8.10-7.30(m,5H,arom), 6.20 (br,2H,NH_2), 2.30(s,3H,CH_3) DMSO.
21a	3600-2900(NH_2,COOH,C-H), 2200(CN), 1660(C=O).	8.40(s,1H,COOH), 6.40(s,2H, NH_2), 1.85(s,3H,CH_3) DMSO.
21b	3420,3310(NH_2), 2980 (C-H), 2200(CN), 1730 (C=O ester), 1620(C=C).	5.50(br,2H,NH_2), 4.40-4.10 (q,2H,CH_2), 2.40(s,3H,CH_3), 1.40-1.10(t,3H,CH_3 ester) DMSO.

a) Uncorrected b) Satisfactory microanalyses obtained: C,+ 0.4%, N, + 0.4%, S,+ 0.2% c) Measured with a PYE Unicam SP 1200 spectrometer d) Measured with a Varian EM 360 L using TMS as internal standard.

In the sequence of our studies only one compound was separated from benzene layer (compound 10). The rest of the prepared products were precipitated during the course of reaction. They were obtained by filtration along with the potassium carbonate layer and the precipitate was washed thoroughly with water and was recrystallized from the appropriate solvent.

In some instances, however, the desired products, compounds 5, 12 and 21a were not found either in the benzene layer nor precipitated during the sequence of reaction. In these cases, the benzene layer was separated and the solid layer was dissolved in water and was treated with dil. HCl whereby they were precipitated, however, compound 21a was not precipitated at once and the aqueous layer was left 3 days at room temperature whereby it was obtained.

Synthesis of compounds 2, 8, 11, 14 *or* 19: 0.05 mole of compounds 1, 7, 10, 12 or 18 in 50 ml ethanol was treated with a catalytic amount of piperidine and was heated at reflux temperature for about 2 hours. The reaction mixture was concentrated and the precipitate was filtered off and was recrystallized from the proper solvents.

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