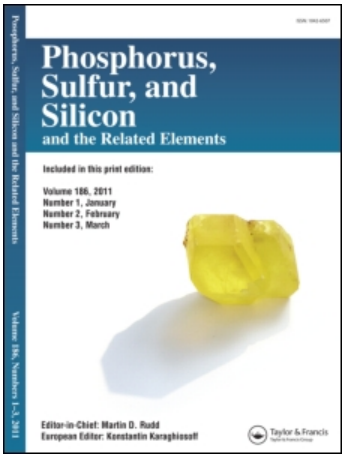

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Application of Phase Transfer Catalysis in Heterocyclic Synthesis: Synthesis of Some New Polyfunctional Thiophenes, Thiopyrans, Pyridines and Oxazines

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APPLICATION OF PHASE TRANSFER CATALYSIS IN HETEROCYCLIC SYNTHESIS: SYNTHESIS OF SOME NEW POLYFUNCTIONAL THIOPHENES, THIOPYRANS, PYRIDINES AND OXAZINES

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Chemistry Department, Faculty of Science, South Valley University, Sohag, Egypt

The reaction of compound ***1*** *with* CS_2 *and different active halo compounds gave the corresponding thiophene derivatives* ***2a,b–4a,b****, whereas treatment of compound* ***1*** *with* CS_2 *and active methylene compounds afforded the corresponding thiopyran derivatives* ***5a,b****,* ***6a,b****,* ***7****, and* ***8****. Also, 1,3-thioxane derivatives* ***9*** *and* ***10*** *were obtained by reacting compound* ***1*** *with* CS_2 *and different cycloalkanones. Thiophene and pyrrolidene derivatives* ***11****,* ***12a,b****, and* ***13a,b*** *were obtained by reacting compound* ***1*** *with phenyl isothiocyanate and different halo compounds. The active methylene compounds and/or cycloalkanones were treated with compound* ***1*** *in the presence of phenyl isothiocyanate to give pyridines, thiopyran and oxazine derivatives* ***14a,b–16a,b****,* ***17a–19a****, and* ***19b****, respectively.*

Keywords: CS_2; diethyl cyanoacetate; ethyl chloroformate; PTC; spiro compounds

Ketoketene[1] or cyanoketene[2] acetals, as well as heterocyclic ketene N, N,[3,4] or N,S-acetals,[3–8] have important applications in heterocyclic synthesis. Our present work deals with the synthesis of new series of thiophenes, thiopyrans, thioxanes, pyridines, and oxazines starting with the related ethyl cyanomalonate, using a solid-liquid phase-transfer catalysis technique.

RESULTS AND DISCUSSION

Diethyl cyanomalonate **1** was synthesized by treating ethyl cyanoacetate with ethyl chloroformate in 1:1 molar ratio using solid-liquid

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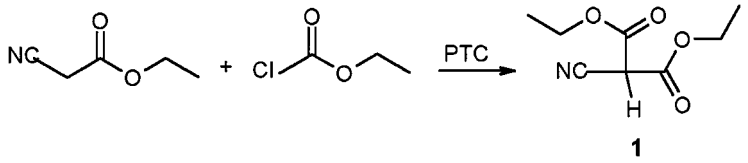
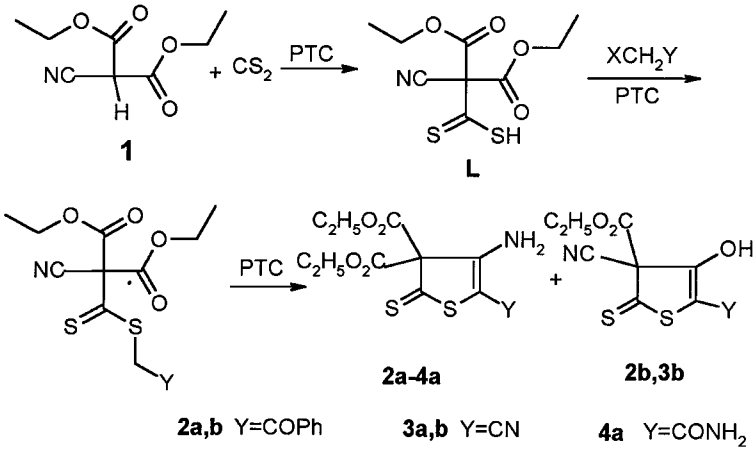
phase-transfer catalysis conditions [benzene/K_2CO_3/tetrabutyl ammonium bromide (TBAB)] (cf. Scheme 1).



SCHEME 1

On treating compound **1** with CS_2 and different halo compounds including phenacyl bromide, chloroacetonitrile, or chloroacetamide in 1:1:1 molar ratio in one pot procedure using solid-liquid PTC conditions [DMF/K_2CO_3/tetrabutylammonium bromide (TBAB)], 3-amino-4-dicarbethoxy thiophene **2a–4a** and 3-hydroxy-4-cyano-4-carbethoxy derivatives **2b**, **3b** were obtained respectively (cf. Scheme 2).

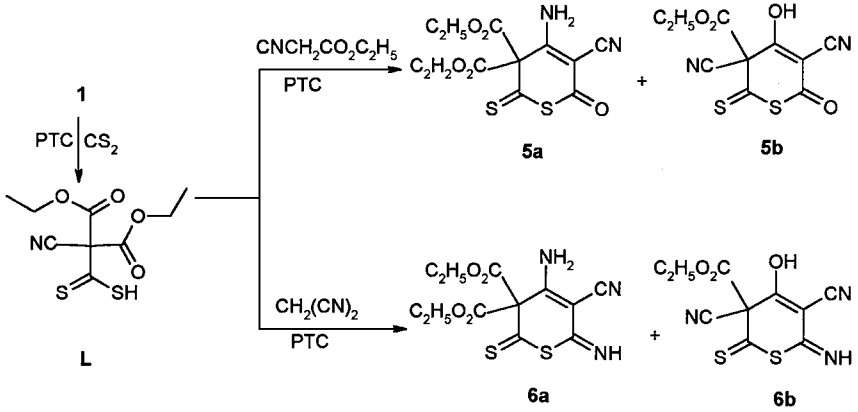


SCHEME 2

The reaction pathway was assumed to proceed through two steps: firstly the formation of dithioic acid[9] (intermediate L) followed by alkylation of the SH group with the halo compound. The second step is either a nucleophilic addition of the active methylene group at the cyano group to form thiophene derivatives **2a** and **4a** or a nucleophilic attack of the active methylene group at the CO ester group with the elimination of an ethanol molecule to give compounds **2b**, **3b** respectively. All products were confirmed by IR, ^{1}H-NMR and elemental analysis.

Treatment of compound **1** with CS_2 and the active methylene compounds ethyl cyanoacetate or malononitrile in a 1:1:1 molar ratio using the same PTC reaction conditions gave the corresponding thiopyran

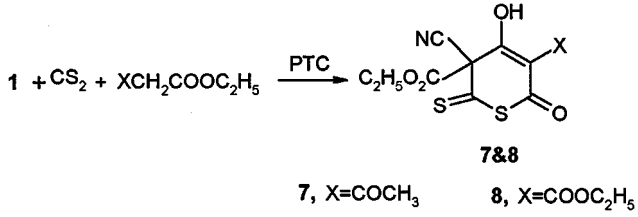
derivatives **5a,b** and **6a,b** respectively. The compounds **5a** and **6a** were obtained from the organic layer in 52% yield and compounds **5b** and **6b** were separated by acidifying the K_2CO_3 layer with dilute acetic acid in 48% yield (cf. Scheme 3).



SCHEME 3

The reaction pathway was assumed to proceed via a nucleophilic attack of the SH group of the dithioic acid at the CO ester group with elimination of an ethanol molecule, followed by cyclization through a nucleophilic attack of the CH_2 group at the cyano group or CO ester group affording compounds **5a** or **5b**. The formation of compounds **6a,b** was assumed to proceed via the attack of the SH group of the dithioic acid at the CN group, followed by another nucleophilic attack of the methylene group at either the cyano group to give compound **6a** or the CO ester group to form compound **6b**.

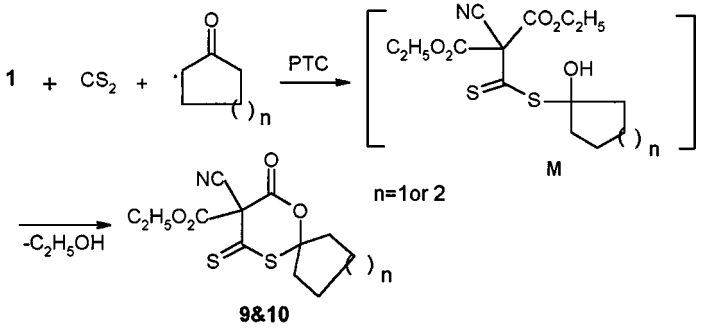
Meanwhile, thiopyran derivatives **7** or **8** were obtained in good yield by reacting compound **1** with CS_2 and ethyl acetoacetate or diethyl malonate in 1:1:1 molar ratio using the same experimental phase-transfer catalysis conditions (cf. Scheme 4).



SCHEME 4

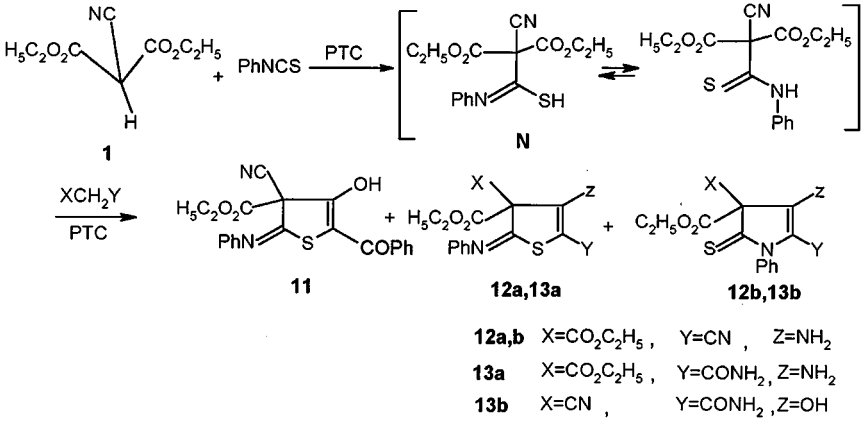
Spiro 1,3-thioxane **9** and **10** were obtained by treating compound **1** with CS_2 and cyclopentanone or cyclohexanone under PTC conditions.

The reaction pathway was assumed to proceed via the attack of the SH group of the intermediate dithioic acid at the CO group to give the adduct M which underwent intramolecular cyclization through the nucleophilic attack of the OH group at the other ethoxycarbonyl group to give the final products **9** or **10** (cf. Scheme 5). IR and ^{1}H-NMR spectra of all the products were consistent with the proposed structures (cf. Table I).



SCHEME 5

Moreover, compound **1** was allowed to react with phenyl isothiocyanate and halo compounds, including chloroacetonitrile, chloroacetamide or phenacyl bromide in 1:1:1 molar ratio under solid liquid, phase-transfer catalysis conditions [DMF/K_2CO_3/tetrabutylammonium bromide (TBAB)] to give the corresponding thiophene derivatives **11**, **12a**, or **13a** as major products and pyrrolidene derivatives **12b** or **13b** as minor ones (cf. Scheme 6).



SCHEME 6

TABLE I Analytical and Spectral Data of the Prepared Compounds

Compound no.	Reaction time (h)	m.p.[a] (crys. solvent)	Yield (%)	$M_F/(M_w)$	Analytical data calc. (found)[b] % C	H	N	S	IR (KBr) ν (cm^{-1})[c]	^{1}H-NMR (DMSO-d_6)[d] δ (ppm)
1	4	305 DMF	73	$C_8H_{11}NO_4$ (185.18)	51.88 (51.40)	5.98 (5.71)	7.56 (7.18)		2988 (CH), 2197 (CN), 1691 (2C=O)	4.3-3.7 (q, 4H, $2CH_2$), 2.9–2.4 (s, 1H, CH), 1.6-1.0 (t, 6H, $2CH_3$)
2a	4	160–162 dioxane	42	$C_{17}H_{17}NS_2O_5$ (379.45)	53.81 (53.32)	4.52 (4.41)	3.69 (3.39)	16.90 (16.71)	3490 (NH_2), 3053 (CH), 2950 (CH), 1700 (2C=O), 1632 (C=O)	8.7-7.0 (m, 5H, arom.), 4.7-4.2 (q, 4H, $2CH_2$), 3.7-3.0 (br, 2H, NH_2), 2.7-1.7 (t, 6H, $2CH_3$)
2b	4	103–105 ethanol	50	$C_{15}H_{11}NS_2O_4$ (333.38)	54.40 (54.53)	3.33 (3.54)	4.20 (4.59)	19.20 (19.41)	3462 (OH), 3066 (CH), 2985 (CH), 2200 (CN), 1700, 1682 (2C=O), 1150 (C=S)	8.3-6.1 (m, 5H, arom.), 4.0-2.8 (q, 2H, CH_2), 2.6-2.3 (s, 1H, OH), 1.6-0.7 (t, 3H, CH_3)
3a	6	200 dioxane	45	$C_{11}H_{12}N_2S_2O_4$ (300.35)	43.99 (43.50)	4.20 (4.22)	9.32 (9.67)	21.34 (21.64)	3427, 3327 (NH_2), 3150 (CH), 2949 (CH), 2187 (CN), 1680 (C=O), 1111 (C=S)	4.7-4.0 (q, 4H, $2CH_2$), 3.8-3.1 (br, 2H, NH_2), 2.2-1.0 (t, 6H, $2CH_3$)
3b	6	220 dioxane	51	$C_9H_6N_2O_3S_2$ (254.29)	42.51 (42.38)	2.38 (2.20)	11.02 (11.18)	25.22 (25.12)	3429 (OH), 2955 (CH), 2195 (CN), 1700 (C=O), 1062 (C=S)	3.7-3.3 (br, 1H, OH), 2.7-2.0 (q, 2H, CH_2), 1.6-1.0 (t, 3H, CH_3)
4a	6	133 ethanol	66	$C_{11}H_{14}N_2S_2O_5$ (318.37)	41.49 (42.25)	4.43 (4.71)	8.79 8.58	20.14 (20.05)	3420, ($2NH_2$), 2951 (CH), 1700, 1645 (3C=O), 1051 (C=S)	5.0-4.3 (br, 2H, NH_2), 3.9-3.4 (br, 2H, NH_2), 3.0-2.3 (q, 4H, $2CH_2$), 1.6-1.0 (t, 6H, $2CH_3$)
5a	5	160 ethanol	52	$C_{12}H_{12}N_2S_2O_5$ (328.36)	43.89 (43.48)	3.68 (3.98)	8.53 (8.73)	19.50 (19.63)	3426, 3326 (NH_2), 2988 (CH), 2212 (CN), 1665 (3C=O), 1180 (C=S)	8.0-7.5 (br, 2H, NH_2), 4.5-3.7 (q, 4H, $2CH_2$), 1.2-0.3 (t, 6H, $2CH_3$)

(Continued on next page)

TABLE I Analytical and Spectral Data of the Prepared Compounds *(Continued)*

Compound no.	Reaction time (h)	m.p.[a] (crys. solvent)	Yield (%)	$M_F/(M_w)$	Analytical data calc. (found)[b] % C	H	N	S	IR (KBr) ν (cm^{-1})[c]	^{1}H-NMR (DMSO-d_6)[d] δ (ppm)
5b	5	166 dioxane	43	$C_{10}H_6N_2S_2O_4$ (282.29)	42.55 (42.06)	2.14 (2.35)	9.92 (9.54)	22.71 (22.84)	3451 (OH), 2992 (CH), 2212 (CN), 1655 (C=O), 1180 (C=S)	4.8-4.1 (q, 2H, CH_2), 4.0-3.7 (s, 1H, OH), 2.0-1.4 (t, 3H, CH_3)
6a	6	240 dioxane	52	$C_{12}H_{13}N_3S_2O_4$ (327.38)	44.03 (44.33)	4.00 (4.13)	12.83 (12.32)	19.58 (19.79)	3449 (NH_2, NH), 2982 (CH), 2197 (CN), 1700 (2C=O), 1093 (C=S)	9.2-8.8 (s, 1H, NH), 4.6-3.2 (q, 4H, $2CH_2$), 3.5-2.9 (br, 2H, NH_2), 1.3-0.3 (t, 6H, $2CH_3$)
6b	6	200 xylene	43	$C_{10}H_7N_3S_2O_3$ (281.30)	42.69 (42.33)	2.50 (2.71)	14.93 (14.78)	22.79 (22.61)	3308 (OH), 3173 (NH), 2210 (CN), 1680 (C=O)	6.2 (s, 1H, NH), 4.8 (s, 1H, OH), 3.5-2.7 (q, 2H, CH_2), 1.1-0.5 (t, 3H, CH_3)
7	6	280 dioxane	68	$C_{11}H_9NS_2O_5$ (299.32)	44.14 (44.56)	3.03 (3.34)	4.68 (4.46)	21.42 (21.55)	3453, 3353 (OH), 2970 (CH), 2201 (CN), 1693 (C=O), 1080 (C=S)	5.0-4.1 (q, 2H, CH_2), 4.0-3.4 (s, H, OH), 2.4 (s, 3H, CH_3), 1.8-0.8 (t, 3H, $3H_3$)
8	6	140 ethanol	71	$C_{12}H_{11}NS_2O_6$ (329.35)	43.76 (44.00)	3.36 (3.67)	4.25 (4.46)	19.46 (19.68)	3451 (OH), 2966 (CH), 2203 (CN), 1682 (C=O), 1088 (C=S)	4.3-3.5 (q, 4H, $2CH_2$), 3.4-3.0 (s, 1H, OH), 2.1-1.0 (t, 6H, $2CH_3$)
9	7	160 ethanol	54	$C_{12}H_{13}NS_2O_4$ (299.36)	48.15 (48.46)	4.37 (4.56)	4.68 (4.88)	21.41 (21.70)	2964 (CH), 2201 (CN), 1680 (C=O), 1086 (C=S)	4.3-3.7 (q, 2H, CH_2), 3.5-2.7 (m, 8H, cyclopentyl), 1.4-0.3 (t, 3H, CH_3)
10	7	304 ethanol	60	$C_{13}H_{15}NS_2O_4$ (313.39)	49.82 (50.30)	4.82 (5.02)	4.46 (4.60)	20.46 (20.67)	3110 (CH), 2970 (CH), 2203 (CN), 1693 (C=O), 1088 (C=S)	4.9-4.0 (q, 2H, CH_2), 2.0-0.7 (t, 13H, CH_3 + cyclohexyl)
11	5	103–105 dioxane	77	$C_{21}H_{16}N_2SO_4$ (392.44)	64.27 (64.40)	4.11 (4.08)	7.14 (7.28)	8.17 (8.28)	3436 (OH), 3060 (CH), 2950 (CH), 2188 (CN), 1652 (C=O)	7.1-6.3 (m, 10H, arom.), 4.1-3.2 (q, 2H, CH_2), 3.0-2.5 (br, H, OH), 1.6-0.9 (t, 3H, CH_3)

12a	6	214 dioxane	39	$C_{17}H_{17}N_3SO_4$ (359.40)	56.81 (56.48)	4.76 (4.65)	11.69 (11.70)	8.92 (9.01)	3420, 3315 (NH_2), 2963 (CH), 2189 (CN), 1687 (C=O)	9.0-7.9 (m, 5H, arom.), 5.2-4.5 (br, 2H, NH_2), 4.4-3.5 (q, 4H, $2CH_2$), 2.4-0.8 (t, 6H, $2CH_3$)
12b	6	292 ethanol	48	$C_{17}H_{17}N_3SO_4$ (359.40)	56.81 (57.1)	4.76 (4.88)	11.69 (11.49)	8.92 (8.74)	3414, 3314 (NH_2), 2945 (CH), 2185 (CN), 1680 (C=O)	9.2-7.6 (m, 5H, arom.), 5.0-3.6 (m, 6H, $2CH_2$ + NH_2), 2.7-1.3 (t, 6H, $2CH_3$)
13a	6	125 ethanol	39	$C_{17}H_{19}N_3SO_5$ (377.42)	54.10 (54.60)	5.07 (5.38)	11.13 (11.34)	8.49 (8.61)	3439, 3300 (NH_2), 2950 (CH), 1670 (C=O), 1620 (C=O), 1200 (C=S)	9.2-8.6 (m, 5H, arom.), 3.8-3.7 (m, 6H, $2CH_2$ + NH_2), 3.2-2.8 (s, 2H, NH_2), 1.5-0.4 (t, 6H, $2CH_3$)
13b	6	201 dioxane	51	$C_{15}H_{13}N_3SO_4$ (331.35)	54.37 (54.76)	3.95 (4.14)	12.68 (12.96)	9.67 (9.86)	3520 (OH), 3429, 3320 (NH_2), 3060 (CH), 2982 (CH), 2199 (CN), 1700 (C=O), 1674 (C=O), 1091 (C=S)	8.5-7.1 (m, 5H, arom.), 4.4-3.7 (q, 2H, CH_2), 3.7-3.2 (s, 2H, NH_2), 3.2-3.0 (s, 1H, OH), 1.3-0.2 (t, 3H, CH_3)
14a	6	285 dioxane	46	$C_{16}H_{12}N_5SO_2$ (338.37)	56.80 (57.00)	3.57 (3.48)	20.70 (20.50)	9.48 (9.62)	3462, 3361 (OH, NH_2), 3110 (CH), 2980 (CH), 2199 (CN), 1689 (C=O), 1093 (C=S)	8.9-8.5 (m, 5H, arom.), 4.2-3.5 (q, 2H, CH_2), 3.4-3.1 (br, 2H, NH+OH), 0.9-0.2 (t, 3H, CH_3)
14b	6	220 dioxane	44	$C_{18}H_{18}N_4SO_4$ (386.43)	55.95 (55.69)	4.70 (4.56)	14.50 (14.68)	8.30 (8.17)	3441, 3340 (NH_2), 3290 (NH), 2964 (CH), 2168 (CN), 1684 (C=O), 1097 (C=S)	9.3-9.0 (br, 1H, NH), 8.6-7.3 (m, 5H, arom.), 4.6-3.8 (q, 4H, $2CH_2$), 3.8-3.1 (br, 2H, NH_2) 1.7-0.5 (t, 6H, $2CH_3$)
15a	6	145 ethanol	35	$C_{18}H_{16}N_2SO_6$ (388.41)	55.56 (55.76)	4.15 (3.03)	7.21 (7.38)	8.6 (8.14)	3422 (OH), 3030 (CH), 2964 (CH), 2191 (CN), 1689 (C=O), 1080 (C=S)	8.7-8.0 (m, 5H, arom.), 7.8-7.2 (br, 1H, OH), 4.5-3.7 (q, 2H, CH_2), 3.5-2.8 (q, 2H, CH_2), 1.5-0.4 (t, 6H, $2CH_3$)

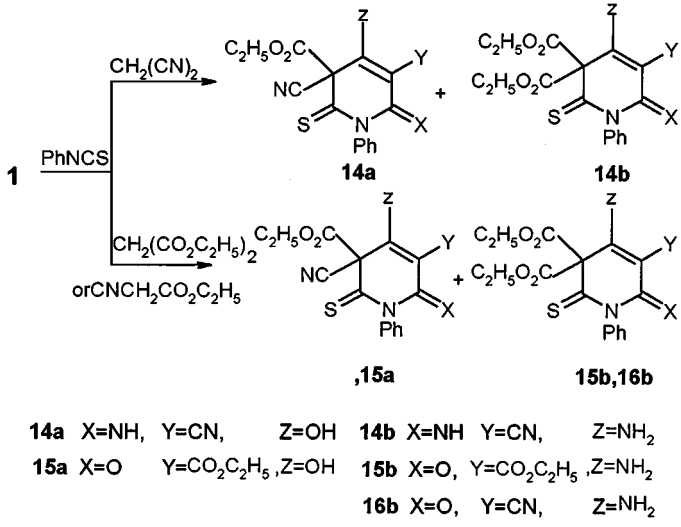
(Continued on next page)

TABLE I Analytical and Spectral Data of the Prepared Compounds *(Continued)*

Compound no.	Reaction time (h)	m.p.[a] (crys. solvent)	Yield (%)	$M_F/(M_w)$	Analytical data calc. (found)[b] % C	H	N	S	IR (KBr) ν (cm^{-1})[c]	^{1}H-NMR (DMSO-d_6)[d] δ(ppm)
15b	6	160 dioxane	62	$C_{20}H_{22}N_2SO_7$ (434.47)	56.61 (57.23)	5.10 (5.30)	6.44 (6.63)	7.37 (7.46)	3429, 3330 (NH_2), 3020 (CH), 2961 (CH), 1700 (C=O), 1064 (C=S)	9.4-8.7 (m, 5H, arom.), 5.0-4.3 (q, 4H, $2CH_2$), 4.1-3.7 (s, 2H, NH_2), 3.3-2.7 (q, 2H, CH_2), 2.3-0.9 (t, 9H, $3CH_3$)
16b	6	185 ethanol	78	$C_{18}H_{17}N_3SO_5$ (387.42)	55.80 55.64	4.42 (4.50)	10.85 (10.64)	8.28 (8.42)	3424, 3330 (NH_2), 3057 (CH), 2978 (CH), 2179 (CN), 1676 (C=O), 1093 (C=S)	8.4-7.2 (m, 5H, arom.), 4.5-3.7 (q, 4H, $2CH_2$), 3.5-2.8 (br, 2H, NH_2), 1.5-0.7 (t, 6H, $2CH_3$)
17	6	263 ethanol	76	$C_9H_6NSO_5$ (240.21)	45.00 (45.40)	2.52 (2.63)	5.83 (6.00)	13.34 (13.44)	3433 (OH), 2980 (CH), 2197 (CN), 1750, 1701 (C=O)	8.7 (s, 1H, CH), 5.0-4.1 (q, 2H, CH_2), 3.9 (s, 1H, OH), 1.7-0.9 (t, 3H, CH_3)
18a	5	285 dioxane	69	$C_{18}H_{18}N_2SO_4$ (358.42)	60.32 (60.50)	5.06 (5.11)	7.81 (7.93)	8.95 (8.72)	2970 (CH), 2197 (CN), 1710 (C=O), 1680 (C=O), 1099 (C=S)	9.0-7.5 (m, 5H, arom.), 4.6-4.0 (q, 2H, CH_2), 4.0-3.7 (t, 4H, $2CH_2$), 3.7-3.0 (m, 4H, $2CH_2$), 1.3-0.7 (t, 3H, CH_3)
19a	5	80 dioxane	33	$C_{19}H_{20}N_2SO_4$ (372.45)	61.27 (61.40)	5.41 (5.22)	7.52 (7.70)	8.61 (8.42)	2953 (CH), 2189 (CN), 1689 (C=O), 1070 (C=S)	8.6-7.7 (m, 5H, arom.), 4.5-4.0 (q, 2H, CH_2), 4.0-3.1 (m, 12H, NH_2 + cyclohexyl), 1.4-1.0 (t, 3H, CH_3)
19b	5	280 ethanol	60	$C_{21}H_{26}N_2SO_5$ (402.51)	62.66 (63.01)	6.51 (6.60)	6.95 (6.76)	7.96 (7.85)	3443 (NH), 3110 (CH), 2957 (CH), 1689 (C=O), 1074 (C=S)	14.1 (s, 1H, NH), 8.5-7.7 (m, 5H, arom.), 4.7-3.9 (q, 4H, $2CH_2$), 3.7-3.0 (m, 10H, cyclohexyl), 1.3-1.0, (t, 6H $2CH_3$)

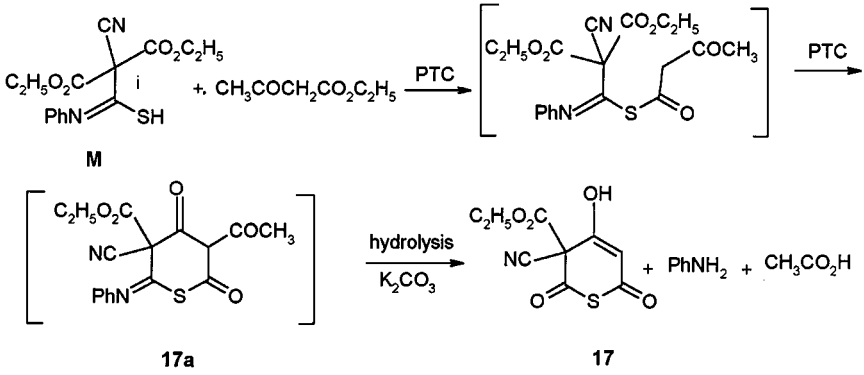
[a]Uncorrected.
[b]Satisfactory microanalysis obtained. ±0.35; H; ±0.4; N; ±0.2; S; ±0.32.
[c]Measured on Nicolet 710 FT-IR spectrophotometer.
[d]Measured by a varian EM 360L spectrometer at 60 MHz using TMS as internal standard and DMSO d_6 as solvent.

Treatment of compound **1** with phenyl isothiocyanate along with the active methylene, malononitrile, diethyl malonate[10] or ethyl cyanoacetate in a 1:1:1 molar ratio, gave the corresponding polyfunctional pyridines **14a**, **b–16a**, **b** (cf. Scheme 7).



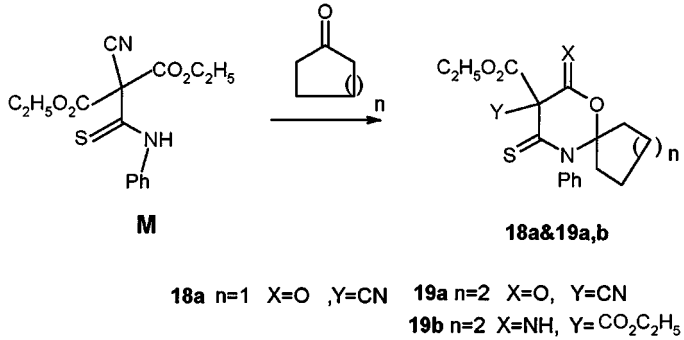
SCHEME 7

On treating compound **1** with phenyl isothiocyanate and ethyl acetoacetate under the usual PTC conditions, the corresponding 3-carbethoxy-3-cyano-4-hydroxythiopyrane 2,5-dione **17** was obtained[11] (cf. Scheme 8).



SCHEME 8

1,3-Oxazine derivatives **18a**,**b** or **19a**,**b** were obtained by treating compound **1** with phenyl isothiocyanate and cyclopentanone or cyclohexanone under the same PTC conditions (cf. Scheme 9).



SCHEME 9

IR and ^{1}H-NMR of all products were in agreement with the suggested structures (cf. Table I).

EXPERIMENTAL

Synthesis of Diethyl Cyanomalonate (1)

A mixture of ethyl cyanoacetate (0.01 mol), ethyl chloroformate (0.01 mol), anhydrous potassium carbonate (3 gm), and a catalytic amount of TBAB, in benzene (20 mL) was stirred for 4 h at 50°C. The reaction mixture was filtered off. The separated carbonate was dissolved in water (60 ml) and filtered. The separated solid was crystallized from ethanol (cf. Table I).

Phase Transfer Catalysis Technique

General Procedure

To a stirred solution of compound **1** (0.01 mol) in dimethylformamide (30 ml) was added anhydrous potassium carbonate (3 g), a catalytic amount of TBAB and (0.01 mol) of CS_2 or phenylisothiocyanate. The formed dianionic ambident compound was then treated with (0.01 mol) of halo compounds (including phenacyl bromide, chloroacetonitrile or chloroacetamide), active methylene compounds (namely, ethyl cyanoacetate, malononitrile, ethyl acetoacetate or diethyl malonate) or cycloalkanone (cyclopentanone or cyclohexanone). The reaction mixture was stirred over periods of time (cf. Table I).

At the end of the reaction (TLC), the organic layer was separated and evaporated in vaccuo. The residue was treated with water, filtered, and crystallized from a suitable solvent, to give **2a,b**, **3a,b**, **4a**, **11**, **12a,b–15b**, **16b**, **19b**, **5a**, and **6a**.

The solid potassium carbonate layer was dissolved in water and filtered. The solid products were crystallized from the suitable solvents, where compounds **12a–15a**, **18**, **19a** were obtained. The filtrate was treated with diluted AcOH and left for 12–24 h at room temperature. The separated solid was filtered off and crystallized from the appropriate solvent, where compounds **5b**, **6b** were obtained.

M.S.—Compound 7: m/e (relative intensity)% : 299(5.30), 292(20.50), 290(98.70), 259(54.90), 190(15.10), 149(39.70).

M.S.—Compound 14a: m/e (relative intensity)% : 339(0.40)(M+1), 307(2.10), 256(13.60), 236(7.10), 185(6.30), 149(18.30).

M.S.—Compound 16b: m/e (relative intensity)% : 388(1.00), 334(5.50), 304(27.1), 142(100), 135(33.90), 118(4.00).

REFERENCES

[1] J. Thuiller and Vialle, *Bull. Soc. Chim. Fr*., 1398 (1959).
[2] G. Kobayashi, Y. Matsuda, and R. Vatsuki, *Chem. Pharm. Bull*. (Tokyo), **21,** 921 (1973).
[3] M. Augustin and W. Doelling, *J. Prakt. Chem*., **324,** 3 (1982).
[4] S. Rajappa and B. G. Advani, *Proc. Indian Acad. Sci. (Chem. Sci*.), **91,** 463 (1982).
[5] K. Hiral, H. Matsuda, and Y. Kishda, *Chem. Pharm. Bull*. (Tokyo), **20,** 97 (1971).
[6] N. B. Mansour, W. D. Rudorf, and M. Z. Augustin, *Z. Fur. Chem*., **21,** 69 (1981).
[7] A. K. El-Shafei, A. M. El-Sayed, and A. M. M. El-Saghier, *Phosphorus, Sulphur, and Silicon*, **90,** 213 (1994).
[8] A. M. El-Sayed, *Phosphorus, Sulphur, and Silicon*, **163,** 29 (2000).
[9] R. Karl Dieter, *Tetrahedron*, **42,** 3029 (1986).
[10] O. A. Abd Allah, *Il Farmaco*, **55,** 641 (2000).
[11] I. R. Bellobono and G. Favini, *Tetrahedron*, **25**(1), 57 (1969).