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EXTRUSION REACTIONS—VII[1]†

FORMATION OF 2,5-DIARYL-1,4-DITHIINS AND 2-ACETONYL THIAZOLES

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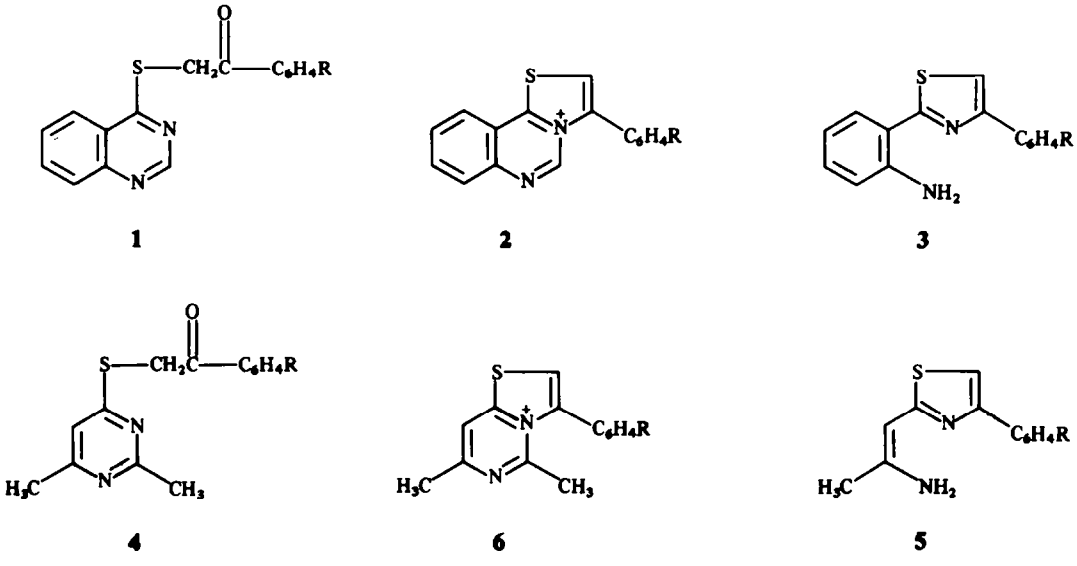
Abstract—ω-(2,6-Dimethyl-4-pyrimidinylthio-(**4**), 2-methyl-4-quinazolinylthio-(**9**), and 4-oxo-2-quinazolinylthio)-(**10**) acetophenones with hydrochloric or perchloric acid provide 2,5-diaryl-1,4-dithiins (**7**) whereas ω-(6-methyl-4-pyrimidinylthio) acetophenones (**11**) with aq $HCl/HClO_4$ or $POCl_3$ followed by hydrolysis provide 1-(4-aryl-2-thiazolyl)-2-propanones (**12**). Likewise, 2-(6-methyl-4-pyrimidinylthio) cyclohexanone (**13**) give the thiazole derivative (**14**).

Heterocyclic cations possessing a C atom between two hetero atoms, with water or an aqueous solution of a base form tetrahedral intermediates which undergo an easy extrusion of this C atom.[2] The isolation of the extruded species from such heterocycles constitutes the basis of the synthesis of a variety of organic compounds.[3-6] During this process the isolation of the residual skeleton of a precursor, as such or in a modified form, would also provide an entry into various categories of organic compounds[7,8] but this concept about such reactions has not been much exploited. We argued that if the parent heterocyclic precursor possesses an appropriately placed functionalized chain which can undergo intramolecular cyclization before or after the ring opening reaction of the cation, such a sequence would provide organic intermediates which otherwise may not be easily available. In one such investigation,[9] we found that ω-(4-quinazolinylthio) acetophenones (**1**), on reaction with aqueous acids form 2(*o*-aminophenyl) thiazoles (**3**) via transient intermediate, thiazolo[3,2-*c*]quinazolin-4-ium cations (**2**). In order to increase the synthetic utility of such 2-substituted thiazoles, it was planned to provide a chemically more pliable handle than an aryl moiety at C(2) of such thiazoles. Following the above sequence of reactions, 4-(pyrimidinylthio) ketones (**4**) would be expected to provide thiazole derivatives (**5**) via thiazolo[3,2-*c*]pyrimidin-4-ium cations (**6**) with a C(2) substituent possessing a chemically valuable enamine moiety at C(2) (Scheme 1). Here, we report the use of the acid catalysed reactions of ω-(4-pyrimidinyl/quinazolinylthio) acetophenones in the synthesis of 2-acetonyl thiazoles and 2,5-diaryl-1,4-dithiins.

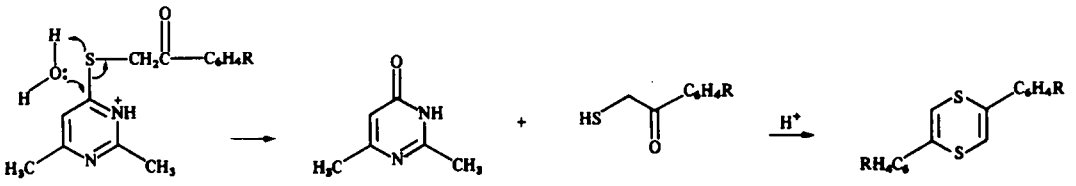
† Dedicated to Prof. P. J. Scheuer, on the occasion of his 70th birthday.

RESULTS AND DISCUSSION

ω-(2,6- Dimethyl -4- pyrimidinylthio)acetophenone (**4**, R = H) with $HCl/HClO_4$ gave a product (~50%), m.p. 110–120°, which possessed sulphur but did not show any test for N and analysed for molecular formula $C_{16}H_{12}S_2$ (MS, $M^{+\cdot}$ *m/e* 268). Its IR spectrum indicated the absence of $>C=O$ and its ^{1}H-NMR



Scheme 1.



Scheme 2.

spectrum exhibited signals at δ 6.47 (2H, s) and 7.17–7.50 (10H, m, ArH). On the basis of these data, the compound has been assigned the structure 2,5-diphenyl-1,4-dithiin (7, R = H) and has been found to be identical with its authentic sample.[10] The aqueous portion of the reaction mixture afforded 2,6-dimethylpyrimidine-4(3H)-one.[11] Thus unlike 1, 4 (R = H) does not undergo cyclohydration and C(2) extrusion to form 5 (R = H) but undergoes an alternate reaction of water at C(4) resulting in the elimination of phenacylthiol which through an acid catalysed bimolecular condensation provides (7, R = H) and the pyrimidine ring remains intact to form pyrimidine-4(3H)-one derivative (Scheme 2).

Likewise, 4 (R = Br, Cl, CH_3, OCH_3) afforded the corresponding dithiins (7) in 45–60% yields (Table 1) along with 2,6-dimethylpyrimidine-4(3H)-one. But ω-(2,6-dimethyl-4-pyrimidinylthio)acetone and ω-(2,6-dimethyl-4-pyrimidinylthio)cyclohexanone failed to provide isolable dithiins probably because of the instability of the alkyl and cycloalkano dithiins.[10] However, the aqueous portions of these reaction mixtures provided 2,6-dimethylpyrimidine-4(3H)-one.

On repeating our earlier report[9] on the reaction of ω-(4-quinazolinylthio)acetophenone (1, R = H) with $HCl/HClO_4$, we again obtained 2(*o*-aminophenyl) thiazole (3, R = H) (75%) along with a small amount of 2,5-diphenyl-1,4-dithiin (7, R = H). ω-(4-Oxo-6-methyl-2-pyrimidinylthio)acetophenones (8, R = H, CH_3) with conc HCl had been reported[12] to provide 7 (R = H, CH_3). At this stage it was evident that in C(2) substituted pyrimidinyl/quinazolinyl-4-thioacetophenones, C(2) extrusion did not find favour probably because of the steric hindrance and an alternate reaction (Scheme 2) took place. Subsequently, we found that ω-(2-methyl-4-quinazolinylthio)-acetophenones 9 (R = H, CH_3, OCH_3) and ω-(4-oxo-2-quinazolinylthio)acetophenones (10, R = H, Cl, Br, CH_3, OCH_3)[13] with aq $HCl/HClO_4$ also provided corresponding 7 (Table 1) along with 2-methylquinazoline-4(3H)-one[14] and quinazoline-2,4(1H,3H)-dione respectively.[15] ω-(2-Pyridylthio)acetophenone[16] with conc $HCl/HClO_4$ remained unchanged. From these results it may be concluded that in such reactions, the elimination of phenacylthiol and the formation of 1,4-dithiins is characteristic of 1,3-diazinyl-2-methyl-4-thioacetophenones and 1,3-diazinyl-2-thioacetophenones.[17]

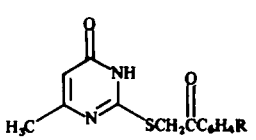
In consequence of the above results, for procuring 5, the reactions of C(2) unsubstituted 4-phenacylthiopyrimidines with $HCl/HClO_4$ were investigated. ω-(6-Methyl-4-pyrimidinylthio)acetophenone (11, R = Cl), on refluxing in hot methanol and $HCl/HClO_4$ (1:1) gave two components. The first fast moving component, m.p. 150–151°, (~15%), was found to be 2,5-diaryl-1,4-dithiin (7, R = Cl). The second component, m.p. 103–106°, (~40%), $M^{+\cdot}$, *m/e* 251, in its IR spectrum showed an absorption band at 1730 (>C=O) cm^{-1}.

Its ^{1}H-NMR spectrum exhibited signals at δ 2.37 (3H, s), 4.17 (2H, s) and 7.32–7.82 (5H, m) and the 2H signal was exchanged with D_2O (overnight) indicating its highly acidic active methylene character. Its ^{13}C-NMR spectrum showed signals at δ 29.69 (q), 47.58 (t) and 202.43 (s) indicating the presence of a $-CH_2COCH_3$ chain.[18] In its mass spectrum, other prominent peaks were present at *m/e* 236 ($251-CH_3$), 208 ($251-COCH_3$), 194 ($251-CH_2COCH_3$) 168 ($ClC_6H_4C_2HS^+$) and 140 ($251-C_6H_5Cl$). All these data were consistent with the structure, 1-[4-(4'-chlorophenyl)-2-thiazolyl]-2-propanone (12, R = Cl). The aqueous portion of the reaction mixture afforded 6-methylpyrimidine-4(3H)-one.[19] Likewise, 11 (R = H, Br, CH_3, OCH_3), gave 12 (R = H, Br, CH_3, CCH_3)

Table 1. 2,5-Diaryl-1,4-dithiins (7)

Product 7	Yield (%) a	b	c	M.p. (°C)	Lit[10] m.p. (°C)
R = H	55	55	50	110–112	116–117
R = CH_3	65	45	45	136–137	136–137
R = OCH_3	60	50	45	131–134	136–137
R = Br	65	—	60	153–155	159–160
R = Cl	60	—	55	152–153	150–151

a, b and c correspond to the yields obtained from the reaction of 10, 9, and 4 respectively.



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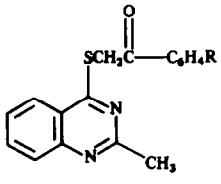

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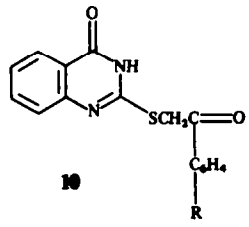

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Table 2. 1-(4-Aryl-2-thiazolyl-2-propanones) (12)

Product	Yield (%) aq. $HCl/HClO_4$	$POCl_3/H_2O$
12 (R = Cl)	40 (15)*	50 (10)*
12 (R = Br)	40 (20)	50 (10)
12 (R = CH_3)	35 (15)	45 (5)
12 (R = OCH_3)	35 (20)	45 (5)
12 (R = H)	40 (15)	50 (5)
14	40	50

* Yields of the corresponding 2,5-diaryl-1,4-dithiins (7).

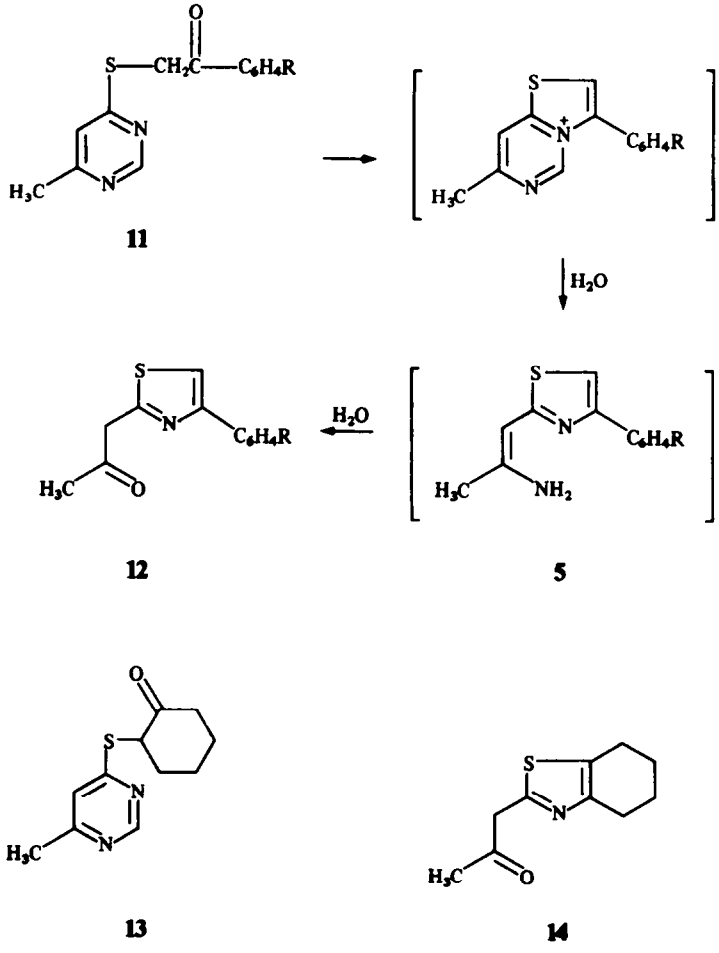
along with the corresponding 7 (Table 2). But 2-(6-methyl-4-pyrimidinylthio) cyclohexanone (13) gave only 4,5,6,7-tetrahydro-2-acetonylbenzothiazole (14) as the dithiin formed here would be unstable. The formation of these products could be rationalized by the mode depicted in Scheme 3.

From the above observations, it was evident that in the reactions of ω-(6-methyl-4-pyrimidinylthio) acetophenones (11) with acid in aqueous medium, the hydrolytic cleavage of phenacylthiol group was in competition with initial cyclodehydration of 11, necessary for the formation of 12. We argued that stepwise procedure involving the cyclodehydration under non-hydrolytic conditions and subsequent hydrolysis of the transient cation, might provide 12 in better yield. Thus ω-(6-methyl-4-pyrimidinylthio) acetophenone (11, R = Cl) was refluxed in phosphoryl chloride for 10–12 hr. After the removal of phosphoryl chloride and treatment with aqueous saturated solution of sodium bicarbonate followed by work up, 12 (R = Cl) was isolated in 50% yield and 1,4-dithiin (7, R = Cl) was formed in negligible amount.[20] Likewise, 11 (R = Br, H, CH_3, OCH_3) and 13 gave corresponding 12 and 14 respectively in better yields (Table 2). ω-(4-Quinazolinylthio)acetophenones (1) under these reaction conditions also give 2-(o-aminophenyl)thiazoles (3)[9] in better yields.[1] However, ω-(2,6-dimethyl-4-pyrimidinylthio)acetophenone derivatives (4) even under these conditions did not undergo a smooth reaction.

The synthetic utility of these 2-acetonylthiazoles (12 and 14), involving C(2) extrusion of their perhydro derivatives and the reactions of the active methylene carbon, is under investigation.

EXPERIMENTAL

M.ps were determined in capillaries and are uncorrected. ^{1}H-NMR were recorded on a Tesla BS 487C 80 MHz instrument using TMS as internal standard. Elemental analyses were performed at the Chemistry Department, Calcutta University, Calcutta, India. IR spectra were recorded



Scheme 3.

with a spectromom 2000 spectrometer. Mass spectra were run on Hitachi Perkin–Elmer RMU-60D and Varian MAT CH-7 instruments. For TLC, plates coated with silica gel G were run in chloroform, ethyl acetate or benzene or their mixtures, and the spots were developed in an iodine chamber.

ω-(2,6-Dimethyl-4-pyrimidinylthio)-acetophenones (4)

ω-Bromoacetophenone (1.99 g, 0.01 mol) in EtOH (10 ml) was added to a stirred soln of 2,6-dimethylpyrimidine-4(3H)-thione[21] (1.40 g, 0.01 mol) in 2% NaOH aq (40 ml). The mixture was stirred overnight. It was diluted with water and was extracted with EtOAc (4 × 50 ml). The extract was washed with water and the solvent was distilled off. The residue was chromatographed over silica gel using benzene to remove excess of ω-bromoacetophenone and then a mixture of benzene–EtOAc to isolate **4** (R = H). Yield 80%, brown coloured semi solid. IR ($CHCl_3$): 1690 (>C=O) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.35 (6H, broad signal, 2 × CH_3), 4.60 (2H, s, CH_2), 6.88 (1H, s, =C—H), 7.44–8.02 (5H, m, ArH). Mass: $M^{+\cdot}$ *m/e* 258; *m/e* 140 (258 − CHCOPh), 107 (140 − SH), 66 (107 $-CH_3-C\equiv N$).

The following compounds were obtained similarly by using appropriate phenacyl halides:

Compound **4** (R = CH_3). Yield 75%, m.p. 95–97°. IR ($CHCl_3$): 1680 (>C=O) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.37 (9H, broad signal, 3 × CH_3), 6.82 (1H, s, =C—H), 4.60 (2H, s, CH_2), 7.22–7.92 (4H, m, ArH). (Found: C, 66.82; H, 5.99; N, 10.75; S, 11.93. Calc for $C_{15}H_{16}N_2OS$: C, 66.18; H, 5.88; N, 10.29; S, 11.76%.)

Compound **4** (R = OCH_3). Yield 70%, m.p. 109–111°. IR ($CHCl_3$): 1675 (>C=O) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.37 (6H, broad signal, 2 × CH_3), 3.85 (3H, s, OCH_3), 4.57 (2H, s, CH_2), 6.00–8.00 (5H, m, ArH, =C—H). (Found: C, 62.97; H, 5.46; N, 9.83; S, 11.55. Calc for $C_{15}H_{16}N_2O_2S$: C, 62.50; H, 5.56; N, 9.76; S, 11.11%.)

Compound **4** (R = Br). Yield 70%, m.p. 126–128°. IR ($CHCl_3$): 1675 (>C=O) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.37 (6H, broad signal, 2 × CH_3), 4.55 (2H, s, CH_2), 6.92 (1H, s, =C—H), 7.62–7.92 (4H, m, ArH). (Found: C, 50.01; H, 4.17; N, 8.23. Calc for $C_{14}H_{13}N_2OSBr$: C, 50.00; H, 3.87; N, 8.33%.)

Compound **4** (R = Cl). Yield 75%, m.p. 105–107°. IR ($CHCl_3$): 1690 (>C=O) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.32 (6H, broad signal, 2 × CH_3), 4.57 (2H, s, CH_2), 6.95 (1H, s, =C—H), 7.47–8.02 (4H, m, ArH). (Found: C, 57.36; H, 4.74; N, 9.75. Calc for $C_{14}H_{13}N_2OSCl$: C, 57.53; H, 4.45; N, 9.93%.)

ω-(2,6-Dimethylpyrimidinylthio)acetone

This was obtained by using chloroacetone in the above procedure. Yield 55%, semisolid. IR ($CHCl_3$): 1725 (>C=O) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.32 (9H, broad signal, 3 × CH_3), 4.02 (2H, s, CH_2), 7.08 (1H, s, =C—H).

ω-(2,6-Dimethyl-4-pyrimidinylthio)-cyclohexanone

Na metal (0.23 g, 0.01 mol) was added to a soln of 2,6-dimethylpyrimidine-4(3H)-thione (1.40 g, 0.01 mol) in absolute EtOH (20 ml). EtOH was removed. The residue was taken in DMF (30 ml) and to its stirred soln, α-chlorocyclohexanone (1.32 g, 0.01 mol), was added dropwise over 10 min. The mixture was stirred overnight. It was diluted with water and was extracted with $CHCl_3$ (4 × 50 ml). The extract was washed with water, dried over Na_2SO_4 and the solvent was distilled off. The residue was chromatographed over silica gel using benzene and a mixture of benzene–EtOAc (8:2) as eluent to give a yellowish brown semisolid, 55%. IR ($CHCl_3$): 1720 (>C=O) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.86–2.76 (14H, m, 2 × CH_3 and cyclohexane H), 4.83 (1H, m, CH), 7.00 (1H, s, =C—H).

ω-(2-Methyl-4-quinazolinylthio)-acetophenones (9)

The following compounds were obtained from 2-methylquinazoline-4(3H)-thione[22] by a procedure similar to the one described for **4**.

Compound **9** (R = H). Yield 60%, semisolid. IR ($CHCl_3$): 1680 (>C=O) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.60 (3H, s, CH_3), 4.85 (2H, s, CH_2), 7.32–8.17 (9H, m, ArH).

Compound **9** (R = CH_3). Yield 55%, m.p. 112–115°. IR ($CHCl_3$): 1670 (>C=O) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.37 (3H, s, CH_3), 2.57 (3H, s, CH_3), 4.72 (2H, s, CH_2), 7.22–8.02 (8H, m, ArH).

Compound **9** (R = OCH_3). Yield 50%, an oil. IR ($CHCl_3$): 1665 (>C=O) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.52 (3H, s, CH_3), 3.77 (3H, s, OCH_3), 4.67 (2H, s, CH_2), 7.40–8.07 (8H, m, ArH).

ω-(6-Methyl-4-pyrimidinylthio)-acetophenones (11)

ω-Bromoacetophenone (1.99 g, 0.01 mol) in EtOH (10 ml) was added to a stirred soln of 6-methylpyrimidine-4(3H)-thione[23] (1.26 g, 0.01 mol) in 2% NaOH aq (40 ml). The reaction mixture was stirred for 6 hr. The solid formed was filtered and was crystallized from EtOH–ether (2:1) to give **11** (R = H). Yield 75%, m.p. 128–129°, IR ($CHCl_3$): 1680 (>C=O) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.37 (3H, s, CH_3), 4.67 (2H, s, CH_2), 7.08 (1H, s, =C—H), 7.35–8.02 (5H, m, ArH), 8.65 (1H, s, =C—H). (Found: N, 11.44. Calc for $C_{13}H_{12}N_2OS$: N, 11.48%.)

Likewise, following compounds were obtained: **11** (R = Cl). Yield 75%, m.p. 155–157°. IR ($CHCl_3$): 1680 (>C=O) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.40 (3H, s, CH_3), 4.65 (2H, s, CH_2), 7.05 (1H, s, =C—H), 7.40–8.02 (4H, m, ArH), 8.70 (1H, s, =C—H). (Found: N, 10.30; S, 11.28. Calc for $C_{13}H_{11}N_2OSCl$: N, 10.07; S, 11.51%.)

Compound **11** (R = Br). Yield 75%, m.p. 160–161°. IR ($CHCl_3$): 1680 (>C=O) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.40 (3H, s, CH_3), 4.62 (2H, s, CH_2), 7.01 (1H, s, =C—H), 7.52–7.95 (4H, m, ArH), 8.67 (1H, s, =C—H). (Found: N, 8.71; S, 9.63. Calc for $C_{13}H_{11}N_2OSBr$: N, 8.67; S, 9.90%.)

Compound **11** (R = CH_3). Yield 65%, m.p. 123–125°. IR ($CHCl_3$): 1680 (>C=O) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.37 (6H, broad signal, 2 × CH_3), 4.67 (2H, s, CH_2), 7.02 (1H, s, =C—H), 7.22–7.99 (4H, m, ArH), 8.72 (1H, s, =C—H). (Found: N, 11.13. Calc for $C_{14}H_{14}N_2OS$: N, 10.85%.)

Compound **11** (R = OCH_3). Yield 65%, m.p. 124–126°. IR

(CHCl$_3$): 1670 (>C=O) cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 2.42 (3H, s, CH$_3$), 3.85 (2H, s, OCH$_3$), 4.67 (2H, s, CH$_2$), 6.90 (1H, s, =C—H), 7.00–8.08 (4H, m, ArH), 8.72 (1H, s, =C—H). (Found: N, 10.49; S, 11.39. Calc for $C_{14}H_{14}N_2O_2S$: N, 10.22; S, 11.68%.)

2-(6-Methyl-4-pyrimidinylthio)-cyclohexanone (13)

This was prepared by the procedure adopted for ω-(2,6-dimethyl-4-pyrimidinylthio)cyclohexanone. 50%, semisolid. IR (CHCl$_3$): 1720 (>C=O) cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 1.82–2.37 (11H, m, CH$_3$ and cyclohexane H), 4.70 (1H, m, CH), 6.90 (1H, s, =C—H), 8.55 (1H, s, =C—H). Mass: M$^{+\cdot}$ *m/e* 222; *m/e* 124 (222 − $C_6H_{10}O$), 83 (124 − CH_3 − C≡N), 56 (83 − HCN).

Reactions of pyrimidinyl/quinazolinylthio-acetophenones with HCl/HClO$_4$

General procedure. A soln of pyrimidinyl/quinazolinylthio-acetophenone (1 g) in methanol (25 ml) containing conc HCl/60% HClO$_4$ (20 ml) was refluxed on a water bath. The progress of the reaction was monitored by TLC of the ethylacetate extracts of the aliquot portions of the mixture after treatment with satd NaHCO$_3$ aq. After the completion of the reaction (TLC), the mixture was cooled, diluted with water (20 ml) and was neutralized with satd NaHCO$_3$ aq. It was extracted with EtOAc. The extract was washed with water and the solvent was distilled off. The residue was chromatographed over silica gel using pet. ether (60–80°)–benzene (1 : 1) as eluent to give the respective dithiins. 2,6-Dimethylpyrimidine-4(3H)-one and quinazoline-2,4(1H,3H)-dione were obtained by the evaporation of water from the aqueous mother liquor of the respective mixtures whereas 2-methylquinazoline-4(3H)-one was isolated from the product mixture extract by chromatography. The following dithiins have been obtained:

Compound 7 (R = H). ^{1}H-NMR (CDCl$_3$): δ 6.52 (2H, s, 2 × =C—H), 7.30–7.55 (10H, m, ArH).

Compound 7 (R = CH$_3$). ^{1}H-NMR (CDCl$_3$): δ 2.30 (6H, s, 2 × CH$_3$), 6.50 (2H, s, 2 × =C—H), 7.08–7.47 (8H, m, ArH).

Compound 7 (R = Cl). ^{1}H-NMR (CDCl$_3$): δ 6.47 (2H, s, 2 × =C—H), 7.17–7.50 (8H, m, ArH).

Compound 7 (R = OCH$_3$). ^{1}H-NMR (CDCl$_3$): δ 3.80 (6H, s, 2 × OCH$_3$), 6.37 (2H, s, 2 × =C—H), 6.87–7.65 (8H, m, ArH).

Compound 7 (R = Br). ^{1}H-NMR (CDCl$_3$): δ 6.50 (2H, s, 2 × =C—H), 7.08–7.88 (8H, m, ArH).

The yields and m.ps of the dithiins have been mentioned in Table 1. The mass spectra of 7 (R = H) and 7 (R = CH$_3$) show fragmentation patterns similar to those reported in the lit.[10]

In similar reactions of 11 (R = H, Cl, Br, CH$_3$, OCH$_3$) with HCl/60% HClO$_4$, 7 (R = H, Cl, Br, CH$_3$, OCH$_3$) were obtained along with 12 (R = H, Cl, Br, CH$_3$, OCH$_3$). These products were separated by column chromatography on silica gel using pet. ether (60–80°)–benzene (1 : 1) and benzene–EtOAc (8 : 2) as eluents while 6-methylpyrimidine-4(3H)-one was obtained by the evaporation of water from the aqueous mother liquor of the reaction mixture. The yields of 7 and 12 are recorded in Table 2 and spectral data for 12 is reported in the following experiment.

Reactions of ω-(6-methyl-4-pyrimidinylthio)-acetophenones (11) *with POCl$_3$*

A soln 11 in freshly distilled POCl$_3$ (20 ml) was refluxed in an oil bath. After 10–12 hr, the mixture was cooled and POCl$_3$ was distilled off at reduced pressure. The residue was taken in hot water (50 ml) and was neutralized with satd NaHCO$_3$ aq. It was extracted with EtOAc (3 × 50 ml) and the extract was washed with water. The extract was dried over Na$_2$SO$_4$ and the solvent was distilled off. The residue consisting of two components was chromatographed over silica gel using pet. ether (60–80°)–benzene (1 : 1) and beazene–EtOAc (8 : 2) as eluents to give the fast moving component, 7, identical with an authentic sample. The second component was found to be 12 (R = H).

Using this procedure, the following compounds were prepared from appropriate derivatives of 11.

Compound 12 (R = Cl) m.p. 103–106°. IR (CHCl$_3$): 1730 (>C=O) cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 2.27 (3H, s, CH$_3$), 4.10 (2H, s, CH$_2$, exchangeable with D$_2$O), 7.30–7.82 (5H, m, ArH and =C—H). Mass: M$^{+\cdot}$ *m/e* 251; *m/e* 236 (251 − CH_3), 208 (251 − $COCH_3$) 194 (251 − $COCH_2CH_3$), 168 ($ClC_6H_4C_2HS^+$).[24]

Compound 12 (R = Br). M.p. 112–115°, IR (CHCl$_3$): 1720 (>C=O) cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 2.30 (3H, s, CH$_3$), 4.15 (2H, s, CH$_2$, exchangeable with D$_2$O), 7.37–7.87 (5H, m, ArH and =C—H). Mass: M$^{+\cdot}$ *m/e* 295; *m/e* 280 (295 − CH_3), 252 (295 − $COCH_3$), 238 (295 − $COCH_2CH_3$), 212 ($BrC_6H_4C_2HS^+$), 140 (295 − C_6H_4 − Br).

Compound 12 (R = CH$_3$). Oil IR (CHCl$_3$): 1710 (>C=O) cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 2.25 (3H, s, CH$_3$), 2.32 (3H, s, CH$_3$), 4.11 (2H, s, CH$_2$, exchangeable with D$_2$O), 7.05–7.77 (5H, m, ArH and =C—H). Mass: M$^{+\cdot}$ *m/e* 231; *m/e* 216 (231 − CH_3), 188 (231 − $COCH_3$), 174 (231 − $COCH_2CH_3$), 148 ($H_3CC_6H_4C_2HS^+$).

1-[*4-Aryl-2-thiazolyl*]-2-*propanone* (12, R = H). Oil. IR (CHCl$_3$): 1720 (>C=O) cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 2.37 (3H, s, CH$_3$), 4.17 (2H, s, CH$_2$, exchangeable with D$_2$O), 7.32–7.82 (6H, m, ArH and =C—H). Mass: M$^{+\cdot}$ *m/e* 217; *m/e* 202 (217 − CH_3), 174 (217 − $COCH_3$) 160 (217 − $COCH_2CH_3$), 134 ($C_6H_5C_2HS^+$).

Compound 12 (R = OCH$_3$). Oil. IR (CHCl$_3$): 1720 (>C=O) cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 2.40 (3H, s, CH$_3$), 3.68 (3H, s, OCH$_3$), 3.85 (2H, s, CH$_2$, exchangeable with D$_2$O), 6.70–7.78 (5H, m, ArH and =C—H). Mass: M$^{+\cdot}$ *m/e* 247; *m/e* 232 (247 − CH_3), 204 (247 − $COCH_3$), 190 (247 − $COCH_2CH_3$), 164 ($H_3COC_6H_4C_2HS^+$), 140 (247 − C_6H_4 − OCH_3).

4,5,6,7-*Tetrahydro-2-acetonyl benzothiazole* 14. Reaction of 13 with HCl/HClO$_4$ or POCl$_3$ followed by work up as described in general procedures gave only one product 14 (TLC), which was purified by chromatography on silica gel using benzene–EtOAc (8 : 2) as eluent. M.p. 123.27°. IR (CHCl$_3$): 1680 (>C=O) cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 1.75–2.07 (4H, m, 2 × CH$_2$), 2.27 (3H, s, CH$_3$), 2.47–3.03 (4H, m, 2 × CH$_2$), 5.52 (2H, s, CH$_2$). Mass: M$^{+\cdot}$ *m/e* 195; *m/e* 180 (195 − CH_3), 152 (195 − $COCH_3$), 138 (195 − $COCH_2CH_3$).

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REFERENCES

[1] Part VI. H. Singh and Kanwal Deep, *Tetrahedron* **40**, 4937 (1984).

[2] O. S. Tee, M. Trani, R. A. McClelland and N. E. Seaman, *J. Am. Chem. Soc.* **104**, 7219 (1982) and refs therein.

[3] A. I. Meyers and E. D. Mihelich, *Angew. Chem. Int. Ed. Engl.* **15**, 270 (1976) and refs therein.

[4] D. Seebach, *Angew. Chem. Int. Ed. Engl.* **18**, 239 (1979).

[5] E. J. Corey and D. C. Boger, *Tetrahedron Letters* 5, 9, 13 (1978).

[6] M. W. Anderson and R. C. F. Jones, *Tetrahedron Letters* **22**, 261 (1981).

[7] D. Gani and D. W. Young, *J. Chem. Soc.* Chem. Commun. 576 (1983).

[8] R. F. Dietrich, T. Sakurai and G. L. Kenyon, *J. Org. Chem.* **44**, 1894 (1979).

[9a] H. Singh, C. S. Gandhi and M. S. Bal, *Indian J. Chem.* **20B**, 17 (1981); [b] H. Singh, C. S. Gandhi and M. S. Bal, *Chem. Ind.* 420 (1980); [c] H. Singh, C. S. Gandhi and M. S. Bal, *Heterocycles* **14**, 3 (1980).

[10] C. M. Buess, V. O. Brandt, R. C. Srivastava and W. R. Carper, *J. Heterocyclic Chem.* **9**, 887 (1972).

[11] H. R. Snyder and H. M. Foster, *J. Am. Chem. Soc.* **76**, 118 (1954).

[12] T. B. Johnson, R. C. Moran and E. F. Kohmann, *J. Am. Chem. Soc.* **35**, 447 (1913).

[13] M. S. Dhatt and K. S. Narang, *J. Indian Chem. Soc.* **31**, 787 (1954).

[14] A. Buzas and C. Hoffman, *Bull. Soc. Chim. Fr.* 1889 (1959); *Chem. Abs.* **54**, 11036a (1960).

[15] M. B. Taylor and G. Scatchard, *J. Am. Chem. Soc.* **41**, 2052 (1919).

[16] C. K. Bradsher and D. F. Lohr, *J. Heterocyclic Chem.* **3**, 27 (1966).

[17] H. Singh, S. K. Aggarwal and N. Malhotra, *Heterocycles* **20**, 983 (1983).

[18] Other signals appeared at δ 114.02(d), 127.507, 128.964, 130.421, 132.994, 134.048(m), 154.230(s) and 161.949(s). The presence of some additional signals might be due to the existence of tautomeric enolic form of **12**.

[19] H. M. Foster and H. R. Snyder, *Organic Synthesis*, Coll. Vol. IV (Edited by N. Rabjohn) p. 638. Wiley, New York (1963).

[20] H. Singh, S. K. Aggarwal and N. Malhotra, *Heterocycles* **22**, 353 (1984).

[21] M. J. F. Brown and H. D. Foster, *Aust. J. Chem.* **19**, 2321 (1966). Instead of pyridine, xylene was used as a solvent.

[22] A. J. Tomisek and B. E. Christensen, *J. Am. Chem. Soc.* **70**, 2423 (1948).

[23] J. R. Marshall and J. Walker, *J. Chem. Soc.* 1004 (1951). It was however, obtained by the reaction of 6-methylpyrimidine-4(3H)-one with P_2S_5 in anhyd xylene.

[24] Q. N. Porter and J. Baldas, *Mass Spectrometry of Heterocyclic Compounds* (Edited by A. Weissberger and E. C. Taylor) p. 532. Wiley, New York (1971).