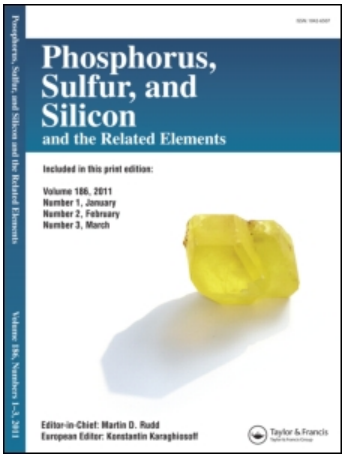

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POLARIZED KETENE DITHIOACETALS—PART II[1]: SYNTHESIS OF S,S- AND S,N-CYCLIC KETENE DITHIOACETALS AND THEIR TRANSFORMATION TO AZOLES AND 1,3-DITHIOLE-2-THIONES[2]

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New procedures for the synthesis of azoles (**3,4**) from 1,3-dithiolanes (**2**), thiazolidinone (**5,6**), thiazolines (**7,9,10**) and 1,3-dithiole-2-thione (**8**) from active methylene compounds (**1a–j**) are described.

Key words: 1,3-Dithiolane; 1,3-dithiane; 1,3-thiazine; 1,3-dithiole-2-thione; thiazoline; ketene dithioacetal.

INTRODUCTION

The S,S- and S,N-ketene dithioacetals are versatile synthons for alternate synthesis of heterocycles,[3] because of the susceptibility of double bonds towards nucleophilic and electrophilic attacks. Functionalized ketene dithioacetals have extensively been employed for the synthesis of various class of heterocycles.[4–9] Polarized cyclic ketene dithioacetals are little explored precursors for the synthesis of azoles and provide an easy access to functionalized heterocycles hitherto obtained by circuitous classical procedures.

RESULTS AND DISCUSSION

Cyclic ketene dithioacetals (**2a,b**) were obtained by alkylation of dithio acid salts derived from methyl acetoacetate with dibromo alkanes.[10] The dithioacid salt was obtained by the condensation of carbon disulphide with methyl acetoacetate (**1e**) in presence of a strong base. The versatality of 1,3-dithiolane (**2a**), a cyclic ketene dithioacetal,[11] was readily recognized by its vulnerability to the attack of hydrazine hydrate and substituted hydrazines to yield functionalized azoles **3** and **4**, respectively. This reaction proceeds through ring opening by attack of nucleophile at highly electrophilic C-2 followed by cyclization to yield pyrazoles (**3,4**). The reaction of active methylene derivatives (**1a–j**) with alkyl/arylisothiocyanate in basic DMF-KOH or in presence of sodium methoxide followed by treatment with ethyl chloroacetate, chloroacetonitrile and propargyl bromide separately yielded thiazolidinones (**5,6**) (Scheme 1) and thiazolines (**7,9** and **10**). A conspicuous deviation was

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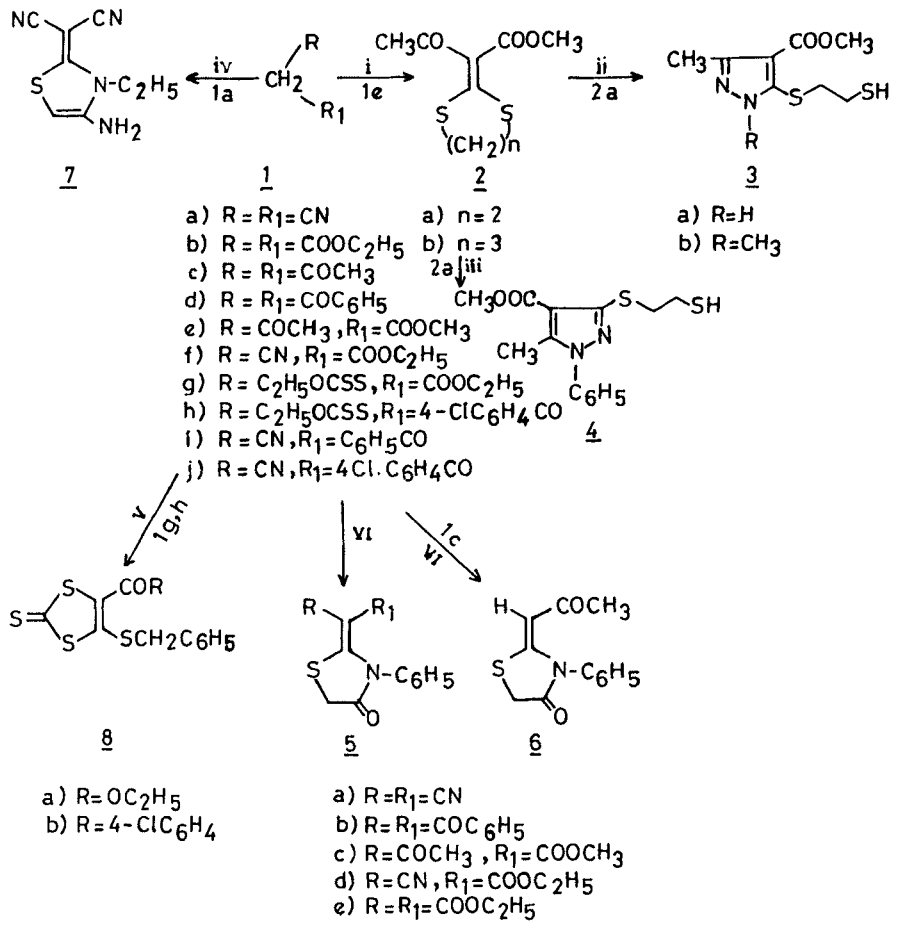
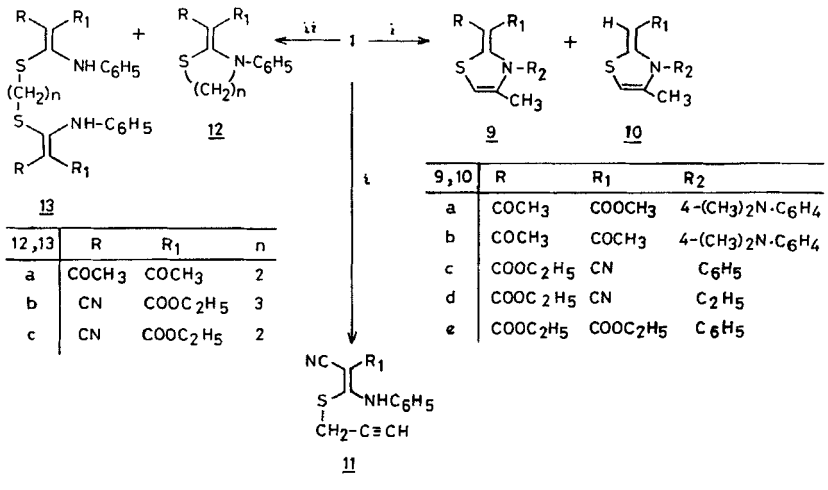


Reagents: i) $K_2CO_3/CS_2/DMF/(CH_2)_n Br_2$ ii) $N_2H_4/CH_3NHNH_2/C_2H_5OH$ iii) $C_6H_5NHNH_2/C_2H_5OH$ iv) $ClCH_2CN/NaOC_2H_5$ v) CS_2 / NaH/ $BrCH_2C_6H_5$ vi) $C_6H_5NCS/NaOC_2H_5/ClCH_2COOC_2H_5$

SCHEME 1

observed in respect of **1c** and **1e** under similar reaction conditions, the former yielded monoacetylated products **6** only, while the latter gave **10a,b** besides normal products **9a,b**. In some cases the reaction of **1i** and **1j** with propargyl bromide yielded only uncyclized products (**11a,b**). Similarly reaction of **1c** and **1f** with phenylisothiocyanate followed by alkylation with dihaloalkanes provided not only the thiazolidenes (**12**, $n = 2$) and 1,3-thiazines (**12**, $n = 3$), but also bis S,N-ketene dithioacetals (**13b,c**) unambiguously characterized (Scheme 2). Reaction of **1g** and **1h** with CS_2 in presence of NaH in DMF followed by alkylation with benzyl bromide did not give the normal S,S-ketene dithioacetal but provided 1,3-dithiole-2-thiones[12-18] **8a,b**. The reaction possibly proceeded via the formation of ketene dithioacetal followed by intra molecular cyclization to yield **8**.



12,13	R	R_1	n
a	$COCH_3$	$COCH_3$	2
b	CN	$COOC_2H_5$	3
c	CN	$COOC_2H_5$	2

9,10	R	R_1	R_2
a	$COCH_3$	$COOCH_3$	$4\text{-}(CH_3)_2N\text{-}C_6H_4$
b	$COCH_3$	$COCH_3$	$4\text{-}(CH_3)_2N\text{-}C_6H_4$
c	$COOC_2H_5$	CN	C_6H_5
d	$COOC_2H_5$	CN	C_2H_5
e	$COOC_2H_5$	$COOC_2H_5$	C_6H_5

a) $R_1 = C_6H_5CO$

b) $R_1 = 4\text{-}ClC_6H_4CO$

Reagents: i) $NaH/R_2NCS/CH{\equiv}C\text{-}CH_2Br$ ii) $NaOC_2H_5/C_6H_5NCS/(CH_2)_nBr_2$

SCHEME 2

EXPERIMENTAL

The melting points were determined in an open capillary are uncorrected. ^1H NMR spectra in $CDCl_3$, unless mentioned otherwise, were obtained on a Perkin Elmer (90 MHz), R-32 spectrometer with TMS as internal standard. The IR spectra were recorded on a Perkin-Elmer Ac-1 spectrometer in KBr. Mass spectra were obtained with a Jeol JMS D-300 spectrometer. The elemental analyses were performed at RSIC, CDRI, Lucknow.

Methyl (1,3-dithiolane-2-ylidene)acetoacetate **2a**: To a mixture of **1e** (1.16 g, 0.01 mole) and K_2CO_3 (4.2 g, 0.03 mol) in DMF (10 ml), CS_2 (0.9 ml, 0.015 mol) was added dropwise under stirring at room temperature and let it stir for an hr. 1,2-Dibromoethane (0.012 mol) was added dropwise to the reaction mixture and was stirred for 6 hr. The content was poured on ice cold water and the precipitate obtained was crystallized from methanol, yield 0.82 g (38%), m.p. 78°C, IR: ν_{max} 1710 (CO) cm $^{-1}$, ^1H NMR: δ 2.42 (s, 3H, CH_3), 3.33 [s, 4H, $(CH_2)_2$], 3.85 (s, 3H, CH_3).

Anal. calcd. for $C_8H_{10}O_3S_2$: C, 44.02; H, 4.62
Found: C, 44.64; H, 4.56.

Methyl (1,3-dithiane-2-ylidene)acetoacetate **2b**: It was prepared from **1e** (1.16 g, 0.01 mol) and 1,3-dibromopropane as described above. The crude product isolated was crystallized from ethyl acetate, yield 1.07 g (46%), m.p. 74°C, IR: ν_{max} 1700 (CO) cm $^{-1}$; m/z 232 (M^+), 217; ^1H NMR: δ 2.14 (s, 2H, CH_2), 2.17 (s, 3H, CH_3), 2.77–3.13 [m, 4H, $(CH_2)_2$], 3.84 (s, 3H, OCH_3).

Anal. calcd. for $C_9H_{12}O_3S_2$: C, 46.53; H, 5.20
Found: C, 47.00; H, 5.04.

3-Methyl-4-methoxycarbonyl-5(2-mercaptoethylthio)-1H-pyrazole **3a**: A mixture of **2a** (0.44 g, 2 mmol) and hydrazine hydrate (0.11 g, 2 mmol) in ethanol (15 ml) was refluxed for 2.5 hr. Excess of solvent was removed under reduced pressure and the residue thus obtained was washed with water and crystallized from ether-hexane, yield 0.45 g (96%), m.p. 98°C, IR: ν_{max} 1720 (CO) cm $^{-1}$; m/z 234 (M^+); ^1H NMR: δ 2.39 (s, 3H, SCH_3), 2.67–2.97 (m, 3H, CH_2SH), 3.21 (t, 2H, SCH_2), 3.72 (s, 3H, OCH_3).

Anal. calcd. for $C_8H_{12}N_2O_2S_2$: C, 41.36; H, 5.21; N, 12.06
Found: C, 41.28; H, 5.29; N, 12.36.

1,3-Dimethyl-4-methoxycarbonyl-5(2-mercaptoethylthio)pyrazole **3b**: It was prepared from **2a** (0.44 g, 2 mmol) and methylhydrazine (0.11 g, 2.1 mmol) as described in the preceding experiment, yield, 0.2

g (40%), oil, IR: ν_{max} 1690 (CO) cm $^{-1}$, m/z 246 (M^+), 245, 213, 203, 185. ^{1}H NMR: δ 2.5 (s, 3H, CH_3), 2.98–3.23 (m, 3H, CH_2SH), 3.37 (t, 2H, SCH_2), 3.72 (s, 3H, N—CH_3), 3.82 (s, 3H, OCH_3).

Anal. calcd. for $C_9H_{14}N_2O_2S_2$: C, 43.87; H, 5.72; N, 11.40
Found: C, 43.42; H, 5.47; N, 11.21.

4-Methoxycarbonyl-5-methyl-3-(2-mercaptoethylthio)-1-phenylpyrazole **4**: It was obtained from **2a** (0.44 g, 2 mmol) and phenylhydrazine (0.25 g, 2 mmol) and worked up as described in the previous experiment, yield 0.24 g (33%), m.p. 92°C, IR: ν_{max} 1700 (CO) cm $^{-1}$, m/z 275 (M^+); ^{1}H NMR: δ 2.53 (s, 3H, CH_3), 2.84–3.22 (m, 3H, CH_2SH), 3.22–3.52 (m, 2H, CH_2), 3.87 (s, 3H, OCH_3), 7.32 (s, 5H, Ar—H).

Anal. calcd. for $C_{14}H_{16}N_2O_2S_2$: C, 54.52; H, 5.23; N, 9.08
Found: C, 54.86; H, 5.12; N, 9.31.

(4-Oxo-3-phenylthiazolidene-2-ylidene)malononitrile **5a**: To a mixture of phenylisothiocyanate (1.35 g, 0.01 mol) and **1a** (0.66 g, 0.01 mol), a solution of sodium ethoxide (10 ml, obtained by dissolving 0.23 g Na in 10 ml of absolute alcohol) was added dropwise under cooling and let the mixture stir for an hr. Ethyl chloroacetate (1.22 g, 0.01 mol) was added to the reaction mixture and stirring was continued overnight. It was poured on cold water and the precipitate thus obtained was filtered and crystallized from chloroform, yield 0.33 g (21%), m.p. 270°C, IR: ν_{max} 1740 (CO), 2200 (CN) cm $^{-1}$, m/z 241 (M^+); ^{1}H NMR: δ 4.27 (s, 2H, CH_2), 7.20–7.60 (m, 5H, Ar—H).

Anal. calcd. for $C_{12}H_7N_3OS$: C, 59.73; H, 2.92; N, 17.41
Found: C, 59.47; H, 2.25; N, 17.32.

(4-Oxo-3-phenylthiazolidene-2-ylidene)dibenzoylmethane **5b**: Yield, 40%, m.p. 250°C, IR: ν_{max} 1700 (CO) cm $^{-1}$, m/z 399 (M^+); ^{1}H NMR: δ 3.80 (s, 2H, CH_2), 7.07–7.7 (m, 15H, Ar—H).

Anal. calcd. for $C_{24}H_{17}NO_3S$: C, 72.16; H, 4.29; N, 3.50
Found: C, 72.79; H, 4.52; N, 3.74.

Methyl (4-oxo-3-phenylthiazolidene-2-ylidene)acetoacetate **5c**: Crystallized from ethyl acetate, yield 30%, m.p. 160°C, IR: ν_{max} 1690 (CO) cm $^{-1}$, m/z 291 (M^+); ^{1}H NMR: δ 2.18 (s, 3H, CH_3), 3.08 (s, 3H, OCH_3), 3.77 (s, 2H, CH_2), 7.08–7.61 (m, 5H, Ar—H).

Anal. calcd. for $C_{14}H_{13}NO_4S$: C, 57.72; H, 4.49; N, 4.83
Found: C, 57.58; H, 4.56; N, 4.48.

Ethyl (4-oxo-3-phenylthiazolidene-2-ylidene)cyanoacetate **5d**: Yield 42%, m.p. 210°C; IR: ν_{max} 1690, 1750 (CO) cm $^{-1}$; m/z 288 (M^+); ^{1}H NMR: δ 1.25 (t, 3H, CH_3), 3.8 (s, 2H, CH_2), 4.20 (q, 2H, CH_2), 7.05–7.30 (m, 2H, Ar—H), 7.35–7.60 (m, 3H, Ar—H).

Anal. calcd. for $C_{14}H_{12}N_2O_3S$: C, 58.31; H, 4.10; N, 9.71
Found: C, 58.41; H, 4.16; N, 9.50.

Diethyl (4-oxo-3-phenylthiazolidene-2-ylidene)malonate **5e**: Purified on silica gel column using ethyl acetate-hexane (1:1) mixture as eluent, yield 60%, m.p. 134°C. IR: ν_{max} 1680, 1730 (CO) cm $^{-1}$, m/z 335 (M^+); ^{1}H NMR: δ 0.9–1.2 (m, 6H, 2 × CH_3), 3.32 (q, 2H, CH_2), 3.74 (s, 2H, CH_2), 4.12 (q, 2H, CH_2), 7.02–7.22 (m, 2H, Ar—H), 7.22–7.44 (m, 3H, Ar—H).

Anal. calcd. for $C_{16}H_{17}NO_5S$: C, 57.29; H, 5.11; N, 4.17
Found: C, 57.34; H, 5.03; N, 4.10.

(4-Oxo-3-phenylthiazolidene-2-ylidene)acetone **6**: It was prepared from **1c** (1.0 g, 0.01 mol), phenylisothiocyanate (1.35 g, 0.01 mol) and ethyl chloroacetate in sodium ethoxide solution as described earlier. The compound thus isolated was characterized as a deacylated product **6**, yield 1.24 g (53%), m.p. 170–72°C. IR: ν_{max} 1720 (CO) cm $^{-1}$; m/z 233 (M^+); ^{1}H NMR: δ 2.01 (s, 3H, $COCH_3$), 3.72 (s, 2H, CH_2), 5.50 (s, 1H), 7.04–7.24 (m, 2H, Ar—H), 7.28–7.60 (m, 3H, Ar—H).

Anal. calcd. for $C_{12}H_{11}NO_2S$: C, 61.78; H, 4.75; N, 6.00
Found: C, 61.84; H, 4.61; N, 6.48.

(4-Amino-3-ethylthiazoline-2-ylidene)malononitrile **7**: It was prepared[19] from **1a** (0.66 g, 0.01 mol) ethylisothiocyanate (0.88 g, 0.01 mol) and chloroacetonitrile (0.75 g, 0.01 mol) as described in the preceding experiment yield (80%), m.p. 210°C, IR: ν_{max} 1650 (CO), 2200 (C≡N), 3410 (NH_2) cm $^{-1}$;

m/z 239 (M^+); ^1H NMR: δ 1.10–1.40 (m, 6H, 2 CH_3), 4.08 (q, 2H, N—CH_2), 4.32 (q, 2H, OCH_2), 5.50 (bs, 2H, NH_2), 5.69 (s, 1H, 5-H).

Anal. calcd. for $C_{10}H_{13}N_3O_2S$: C, 50.19; H, 5.47; N, 17.56
Found: C, 50.34; H, 5.62; N, 17.82.

4-Benzylthio-5-ethoxycarbonyl-1,3-dithiole-2-thione **8a**: To a cold reaction mixture of **1g** (0.42 g, 2 mmol) and CS_2 (0.15 g, 2 mmol), NaH (0.1 gm, 50% dispersion) was added portionwise and allowed to stir for 2 hr. Benzyl bromide (0.68 g, 4 mmol) was added to this reaction mixture maintaining the temperature at −10°C, continuing the stirring for 3 hr and left overnight. The reaction mixture was poured on crushed ice with stirring and the solid obtained was filtered and crystallized from ethyl acetate-hexane, yield 0.3 g, (46%), m.p. 105°C. IR: ν_{max} 1685 cm^{-1} (CO): m/z 328 (M^+), 284, 181, 119; ^1H NMR: 1.45 (t, 3H, CH_3), 4.20 (s, 2H, CH_2), 4.45 (q, 2H, CH_2), 7.35–7.52 (m, 5H, Ar—H).

Anal. calcd. for $C_{13}H_{12}O_2S_4$: C, 47.52; H, 3.65
Found: C, 48.00; H, 3.67.

4-Benzylthio-5-(4-chlorobenzoyl)-1,3-dithiole-2-thione **8b**: It was prepared from **1h** (0.55 g, 2 mmol) as described in the preceding experiment, yield 0.25 g, (63.3%), m.p. 95°C, IR: ν_{max} 1640 (CO) cm^{-1}; m/z 394 (M^+), 361, 300. ^1H NMR: 4.15 (s, 2H, CH_2), 7.27–7.37 (m, 5H, Ar—H), 7.42 (d, 2H, Ar—H), 7.66 (d, 2H, Ar—H).

Anal. calcd. for $C_{17}H_{11}ClOS_4$: C, 51.69; H, 2.80
Found: C, 51.38; H, 3.31.

Methyl [3-(4-dimethylaminophenyl)-4-methylthiazoline-2-ylidene]acetoacetate/acetate **9a, 10a**: To an ice cold suspension of NaH (0.02 mol, 50% dispersion) in dry DMF (10 ml), a solution of methyl acetoacetate (1.16 g, 0.01 mol) in DMF (2 ml), followed by 4-dimethylaminophenylisothiocyanate (1.78 g, 0.01 mol) were added. The reaction mixture was stirred for 2 hr, followed by gradual addition of propargyl bromide (1.2 g, 0.01 mol) within 30 minutes. The stirring was continued for additional 2 hr and the contents poured on cold water. The aqueous phase was extracted from chloroform, dried and purified on silica gel column using chloroform:hexane (1:1) as eluent. Two compounds thus isolated from the column were characterized as **9a**: yield 0.23 g (7%), m.p. 154°C; IR: ν_{max} 1700 (CO) cm^{-1}, m/z 326 (M^+). ^1H NMR: 1.93 (s, 3H, CH_3), 2.21 (s, 3H, $COOCH_3$), 3.00 (s, 6H, $N(CH_3)_2$), 3.15 (s, 3H, OCH_3), 6.33 (s, 1H, 5-H), 6.65 (d, 2H, Ar—H), 6.96 (d, 2H, Ar—H).

Anal. calcd. for $C_{17}H_{20}N_2O_3S$: C, 61.45; H, 6.02; N, 8.43
Found: C, 62.31; H, 6.28; N, 8.48.

10a: Yield 0.69 (21%), m.p. 208–210°C; IR: ν_{max} 1640 (CO) cm^{-1}, m/z 290 (M^+), 259, 231; ^1H NMR: δ 1.80 (s, 3H, CH_3), 2.94 (s, 6H, $N(CH_3)_2$), 3.57 (s, 3H, OCH_3), 4.64 (s, 1H), 5.84 (s, 1H, 5-H), 6.67 (d, 2H, Ar—H), 6.95 (d, 2H, Ar—H).

Anal. calcd. for $C_{15}H_{18}N_2O_2S$ (290.37): calcd. C, 62.04; H, 6.24; N, 9.64
Found: C, 62.07; H, 6.18; N, 9.73.

9b: Yield 0.15 g (5%), m.p. 163–65°C; IR: ν_{max} 1645 (CO) cm^{-1}, m/z 316 (M^+), 301, 273; ^1H NMR: δ 2.0 (s, 3H, CH_3), 2.02 (s, 6H, CH_3), 3.01 (s, 6H, $N(CH_3)_2$), 6.46 (s, 1H, 5-H), 6.65 (d, 2H, Ar—H), 6.90 (d, 2H, Ar—H).

Anal. calcd. for $C_{17}H_{20}N_2O_2S$: C, 64.52; H, 6.37; N, 8.85
Found: C, 64.31; H, 6.28; N, 8.91.

10b: Yield 0.63 g (23%), m.p. 210°C; m/z 274 (M^+), 259, 243; ^1H NMR: δ 1.90 (s, 3H, CH_3), 2.01, (s, 3H, $COCH_3$), 3.04 (s, 6H, $N(CH_3)_2$), 5.34 (s, 1H), 6.05 (s, 1H, 5-H), 6.75 (d, 2H, Ar—H), 7.04 (d, 2H, Ar—H).

Anal. calcd. for $C_{15}H_{18}N_2OS$: C, 65.65; H, 6.61; N, 10.21
Found: C, 65.73; H, 6.57; N, 10.18.

9c: Yield 43%, m.p. 190°C; IR: ν_{max} 1680 (CO), 2190 (C≡N) cm^{-1} m/z 286 (M^+), 241, 213; ^1H NMR: δ 1.26 (t, 3H, CH_3), 1.90 (s, 3H, CH_3), 4.21 (q, 2H, CH_2), 6.40 (s, 1H, 5-H), 7.20–7.35 (m, 2H, Ar—H), 7.41–7.60 (m, 3H, Ar—H).

Anal. calcd. for $C_{15}H_{14}N_2O_2S$: C, 62.91; H, 4.92; N, 9.78
Found: C, 62.87; H, 4.81; N, 9.80.

9d: Yield 45%, m.p. 132°C; IR: ν_{max} 1650 (CO), 2200 (C≡N) cm^{-1}, m/z 238 (M^+), 193, 165; ^1H NMR: δ 1.23–1.43 (m, 6H, CH_3) 2.32 (s, 3H, CH_3), 4.02–4.50 (m, 4H, CH_2), 6.37 (s, 1H, 5-H).

Anal. calcd. for $C_{11}H_{14}N_2O_2S$: C, 55.43; H, 5.92; N, 11.75
Found: C, 55.49; H, 5.97; N, 11.73.

9e: Yield 35%, m.p. 103–105°C; IR: ν_{max} 1690 (CO) cm^{-1}, m/z 333 (M^+), 323. ^1H NMR: δ 1.4 (t, 6H, CH_3), 1.82 (s, 3H, CH_3), 3.81 (q, 4H, CH_2), 6.25 (s, 1H, 5-H), 7.12–7.31 (m, 2H, Ar—H), 7.31–7.59 (m, 3H, Ar—H).

Anal. calcd. for $C_{17}H_{19}NO_4S$: C, 61.24; H, 5.74; N, 4.19
Found: C, 61.31; H, 5.73; N, 4.17.

2-Benzoyl-3-phenylamino-3-propargylthioacrylonitrile **11a**: To a solution of benzoylacetonitrile (0.29 g, 2 mmol) in dry DMF (5 ml), NaH (50 mg, 50% dispersion in mineral oil) was added portionwise under stirring. After 1 hr phenylisothiocyanate (0.27 g, 2 mmol) was added and the resulting mixture was stirred for another hr. Propargyl bromide (0.24 g, 0.2 mmol) was then added and stirring continued for 3 hr, and the contents poured on crushed ice with vigorous stirring. The precipitate thus obtained was filtered, washed with water and crystallized from ethyl acetate, yield 0.62 g (22%), m.p. 122°C, IR: ν_{max} 2180 (C≡N) cm^{-1}, m/z 318 (M^+); ^1H NMR: δ 2.34 (t, 1H, ≡CH), 3.57 (d, 2H, CH_2), 7.23–7.55 (m, 8H, Ar—H), 7.65–8.02 (m, 2H, Ar—H).

Anal. calcd. for $C_{19}H_{14}N_2OS$: C, 71.67; H, 4.43; N, 8.80
Found: C, 71.68; H, 4.48; N, 8.85.

2-(4-Chlorobenzoyl)-3-phenylamino-3-propargylthioacrylonitrile **11b**: Yield 0.6 g (17%); IR: ν_{max} 2200 (C≡N) cm^{-1}, m/z 352 (M^+), ^1H NMR: 2.31 (t, 1H, ≡CH), 3.55 (d, 2H, CH_2), 7.21–7.51 (m, 7H, Ar—H), 7.81 (d, 2H, Ar—H).

Anal. calcd. for $C_{19}H_{13}ClN_2OS$: C, 64.68; H, 3.71; N, 7.94
Found: C, 64.46; H, 3.68; N, 8.05.

(3-Phenylthiazolidine-2-ylidene)acetylacetone **12a**:

Procedure A: To a cold suspension of finely ground KOH (0.56 g, 0.01 mol) in DMF (10 ml), acetylacetone (1 g, 0.01 mol) was added. After half an hr phenylisothiocyanate (1.35 g, 0.01 mol) was added. The resulting mixture was then treated with dibromoethane (1.88 g, 0.01 mol) dropwise and stirring continued for 24 hr. It was then poured on crushed ice, extracted with chloroform and subjected to column chromatography using hexane-ethyl acetate (9:1) as eluent, yield 0.42 g (16%), m.p. 54°C, IR: ν_{max} 1720 (CO) cm^{-1}, m/z 261 (M^+); ^1H NMR: δ 2.05 (s, 6H, $2CH_3$), 2.85 (s, 2H, SCH_2), 2.91 (s, 2H, NH_2), 7.0–7.30 (m, 2H, Ar—H), 7.35–7.60 (m, 3H, Ar—H).

Anal. calcd. for $C_{14}H_{15}NO_2S$: C, 64.34; H, 5.78; N, 5.35
Found: C, 64.22; H, 5.69; N, 5.41.

Procedure B: To a cold solution of **1f** (1 g, 0.01 mol) in sodium ethoxide (obtained from 0.23 Na in 10 ml of ethanol), phenylisothiocyanate (1.13 g, 0.01 mol) was added. After 1 hr of stirring, dibromopropane (2.02 g, 0.01 mol) was added and left overnight. It was poured on cold water, extracted with chloroform and purified on silica gel column using hexane-ethyl acetate (9:1) as eluent. Two products were isolated and the first was characterized as **12b**; yield 0.61 g (21%); m.p. 60°C, IR: ν_{max} 1650 (CO), 2200 (C≡N) cm^{-1}, m/z 288 (M^+); ^1H NMR: δ 1.26 (t, 3H, CH_3), 2.02 (q, 2H, CH_2), 2.80 (t, 2H, SCH_2), 3.29 (t, 2H, NCH_2), 4.25 (q, 2H, OCH_2), 7.35 (s, 5H, Ar—H).

Anal. calcd. for $C_{15}H_{16}N_2O_2S$: C, 62.47; H, 5.59; N, 9.71
Found: C, 62.72; H, 5.41; N, 9.81.

The second product, was characterized as **13b**, yield 0.36 g (7%), m.p. 96–98°C; IR: ν_{max} 1640 (CO), 2200 (C≡N) cm^{-1}; m/z 536 (M^+). ^1H NMR: δ 1.32 (t, 6H, CH_3), 1.69 (t, 2H, CH_2), 2.58 (t, 4H, 2 SCH_2), 4.22 (q, 4H, 2 × OCH_2), 7.20 (s, 10H, Ar—H).

Anal. calcd. for $C_{27}H_{28}N_4O_4S_2$: C, 60.44; H, 5.26; N, 10.44
Found: C, 60.46; H, 5.27; N, 10.42.

13c: It was prepared from **1f** (1.13 g, 0.01 mol), phenylisothiocyanate (1.35 g, 0.01 mol) and dibromoethane (1.88 g, 0.01 mol) as described in the preceding experiment which exclusively provided **13c**, yield 1.51 g (29%), m.p. 180°C, IR: ν_{max} 1640 (CO), 2190 (C≡N) cm^{-1}, m/z 522 (M^+).

Anal. calcd. for $C_{26}H_{26}N_4O_4S_2$: C, 59.75; H, 5.01; N, 10.72
Found: C, 59.70; H, 4.96; N, 10.78.

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