

Reactions of 3-substituted 5-arylmethylene-1, 3-Thiazolidin-2, 4-diones with Azide and Cyanide Ions

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Abstract: Sodium azide reacted with 3-substituted-5-arylmethylene-1, 3-thiazolidines 3a-d to give the pyrazolinone derivatives 7a-d as well as the 3-unsubstituted-1, 3-thiazolidine derivative 3f and the cinnamate salt 8a in case of 3d. However, 3e gave the 3-unsubstituted-1, 3-thiazolidin-2, 4-dione derivative 3g and the cinnamate salt 8b. Reactions of potassium cyanide with 3b-e yielded a mixture of butyronitrile derivative 9, 3f, 3g and a water soluble adduct that yielded 10 upon treating with chloroacetic acid, as well as 2-oxo-but-3-enitrile derivative 11 in case of 3e. Structures of all products were evidenced by microanalytical and spectral data.

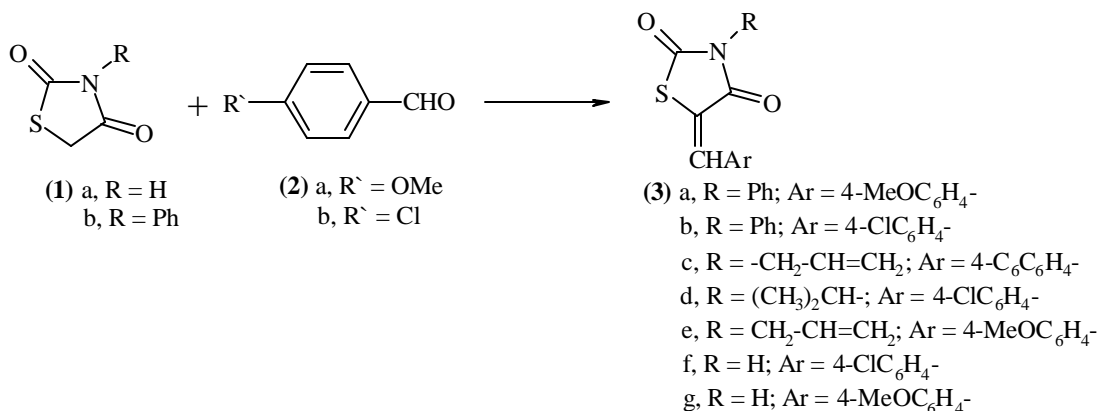
Key words: Pyridazine derivatives • 5-arylmethylene-1, 3-thiazolidin-2, 4-diones • pyrazolinone derivatives • butyronitrile derivative, 2-oxo-but-3-enitrile

INTRODUCTION

It has been reported [1-4] that 3-substituted-5-arylmethylene-1, 3-thiazolidin-2, 4-diones react with hydrazines, morpholine, benzylamine and piperidine to afford pyrazolinones, thiolpropenamides, arylamino-carboxamide and N-phenylacrylamide derivatives, respectively. However, the 3-unsubstituted derivatives gave upon treatment with hydrazine hydrate and piperidine the corresponding triazinone [3, 5] and acrylamide derivatives [6]. The latent ability of this ring system to cleave at 1, 2-as well as 3, 4-bonds encourage us to synthesize some 3-substituted 5-arylmethylene-1, 3-thiazolidin-2, 4-diones to investigate the behaviour of this ring towards azide and cyanide ions that had never been studied before.

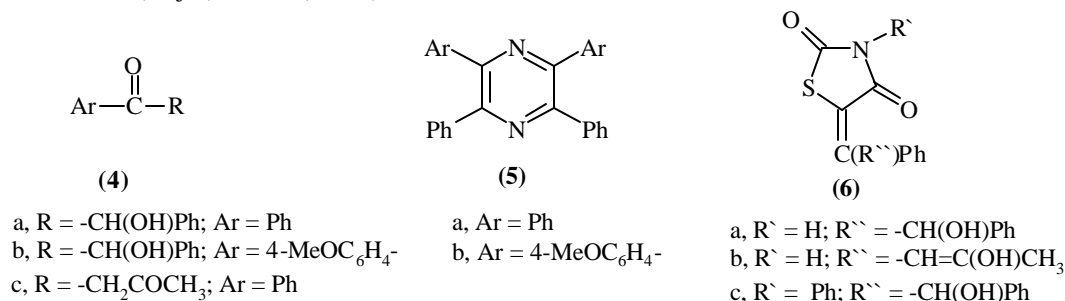
RESULTS AND DISCUSSION

The starting materials (3a, b) were synthesized by condensing 3-phenyl-1, 3-thiazolidin-2, 4-dione (1b) with the appropriate aldehyde using sodium acetate-acetic acid [6]. However, (3c-e) were prepared following the method of Lo *et al.* [7] by treating the potassium salt of the respective N-unsubstituted analogues; obtained from 1, 3-thiazolidin-2, 4-dione 1a and the appropriate aldehyde with allyl or isopropyl bromide in dimethylformamide and were shown to be mixtures of the (E) and (Z)-isomers [3]. In the present study, the (E, Z)-mixtures were used without separation.



Unfortunately, attempts to prepare new arylidene thiazolidin-2, 4-diones through condensation of (1a, b) with benzoin (4a), 4-methoxybenzoin (4b) and benzoylacetone (4c) gave a poor yield of adducts.

Thus reacting equimolar amounts of 1, 3-thiazolidin-2, 4-dione (1a) with benzoin (4a), 4-methoxybenzoin (4b) or benzoylacetone (4c) in refluxing toluene in presence of ammonium acetate as a base, afforded a mixture of 5a (major) and 6a (minor), 5b or 6b, respectively. Similar treatment of 3-phenyl-1, 3-thiazolidin-2, 4-dione (1b) with 4a gave a mixture of 5a (major) and 6c (minor).

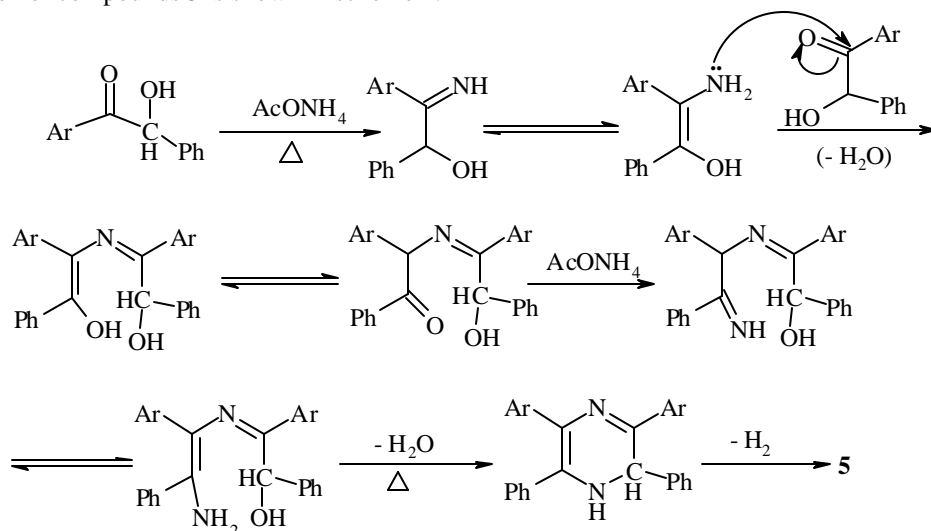


The structures of compounds 5 and 6 were evidenced from their analytical and spectral data. The infrared spectra of 5 showed absorption bands corresponding to C = N and/or C = C. However, those of compounds 6 exhibited stretching absorptions assignable to NH and/or OH as well as two strong absorptions, characteristic of C = O in the respective systems. The ¹H-NMR spectra of compounds 5 and 6 were in accord with the proposed structures. Compound 5b exhibited a singlet signal for methoxy protons. However, compounds 6 revealed exchangeable singlets for OH and/or NH protons as well as singlet signals for methine protons. The downfield value for OH proton signal of compounds 6a, c suggested the existence of chelation with the 5-oxo group of the heteroring. Further evidence was gained from EI-MS spectra that showed the molecular ion peaks for compounds 5. However, the EI-MS spectra of compounds 6 didn't show the molecular ion peaks, instead they

showed ($M^+ - \begin{matrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{S} - \text{NH} \end{matrix}$) peak for compounds 6a, c and ($M^+ - \text{HNCO} - \text{CH} = \text{C}(\text{OH})\text{CH}_3$) peak.

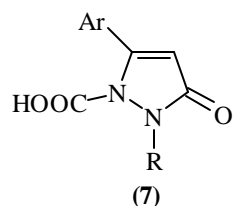
In case of 6b, beside some of abundant peaks.

The formation of compounds 5 is shown in scheme 1.

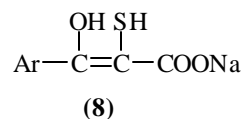


Scheme 1

The treatment of (E, Z)-3-substituted-5-arylmethylene-1, 3-thiazolidin-2, 4-diones 3a-d with sodium azide (3 equiv.) in refluxing dimethylformamide afforded the pyrazolinone derivatives 7a-d (major) as well as 3f and the 4-chlorocinnamate salt derivative 8a in minor amount in case of 3d. Similar treatment of 3e with sodium azide yielded only 3g and 8b.

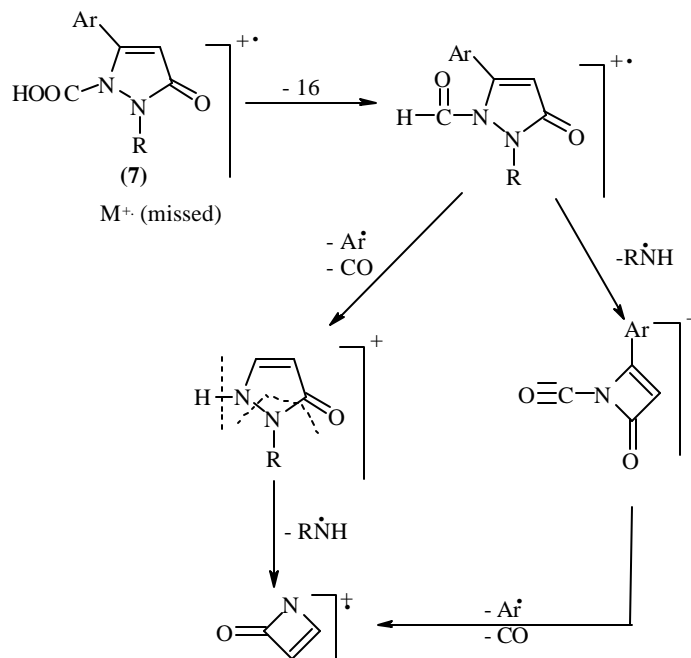


- a, R = Ph; Ar = 4-MeOC₆H₄-
 b, R = Ph; Ar = 4-ClC₆H₄-
 c, R = -CH₂-CH=CH₂; Ar = 4-ClC₆H₄-
 d, R = (CH₃)₂CH-; Ar = 4-ClC₆H₄-



- a, Ar = 4-ClC₆H₄-
 b, Ar = 4-MeOC₆H₄-

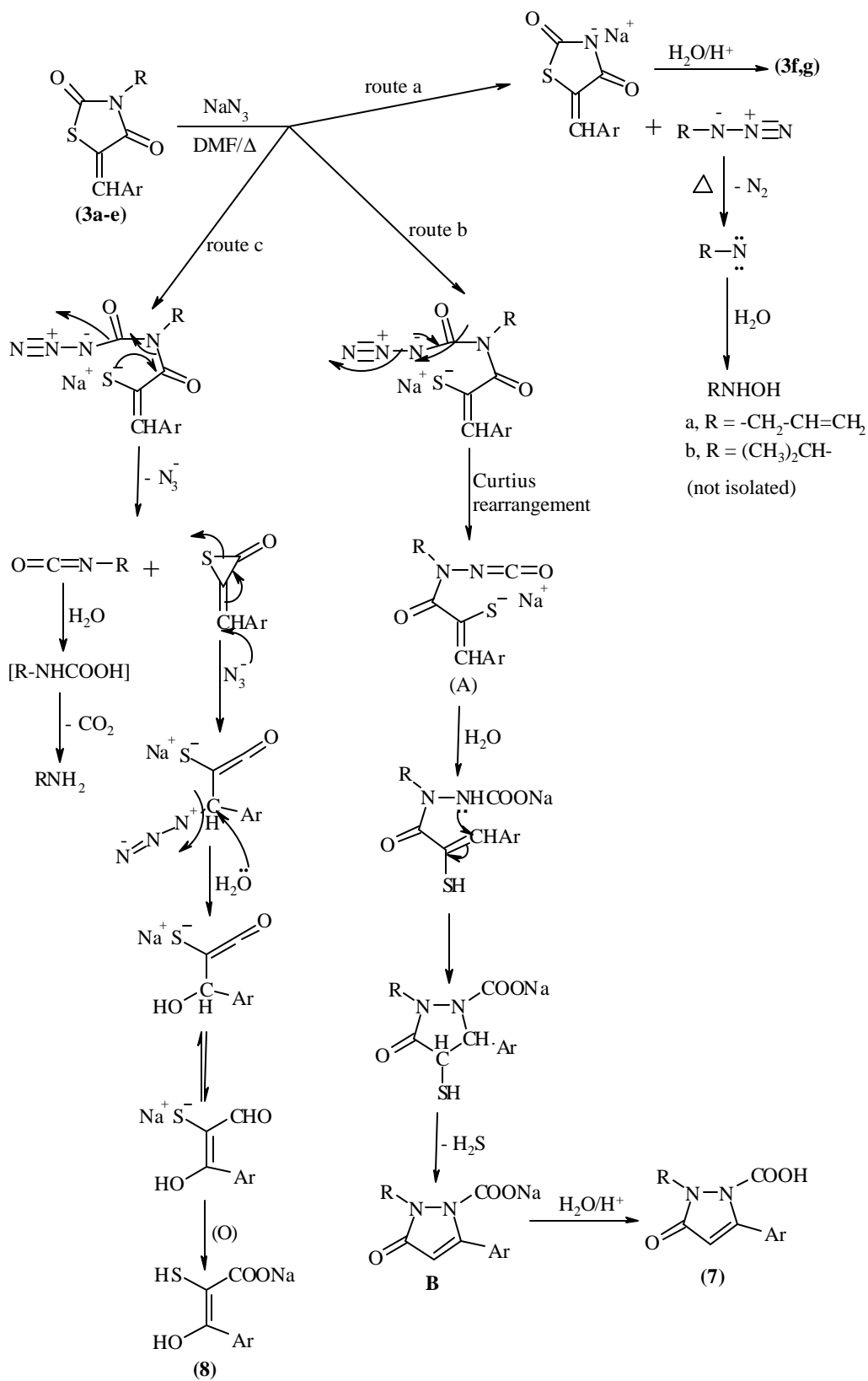
The structure of compounds 7a-d was substantiated from their analytical and spectral data. Their infrared spectra showed stretching absorptions assignable to OH, C = O and C = C groups of pyrazolinones [8]. The ¹H-NMR spectra of 7 were in good agreement with the suggested structure. Further evidence was gained from their EI-MS where they didn't show the molecular ion peak, instead a peak corresponding to M⁺ - 16. The fragmentation pathway of compounds 7 is shown in scheme 2.



Scheme 2

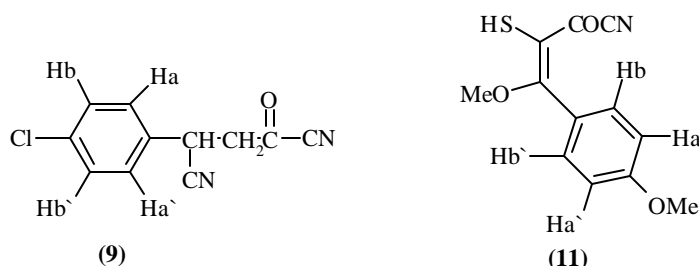
The structure of compounds 3f and 3g was rigidly confirmed by mixture m.p. with authentic samples. However, the structure of compounds 8a, b was based only on the infrared spectra due to the poor yields.

The formation of compounds 3, 7 and 8 (Cf. scheme 3) could be rationalized on the basis of attack of azide ion at allyl or isopropyl group to afford compounds 3f and 3g (route a). Thiazolidine ring opening through attack of azide ion at the 2-oxo-group followed by Curtius rearrangement gave the isocyanate intermediate (A). Successive hydrolysis, intramolecular cyclization followed by elimination of hydrogen sulfide afforded the pyrazolinone salt B (route b). Acidification of B gave compound 7. Route c involves attack by azide ion at the 2-oxo-group of the hetero ring followed by 3, 4-cleavage to give thirane and isocyanate intermediates. Thirane ring opening through attack by another azide ion at the β-carbon of the exocyclic double bond followed by successive hydrolysis and oxidation yielded compound 8.



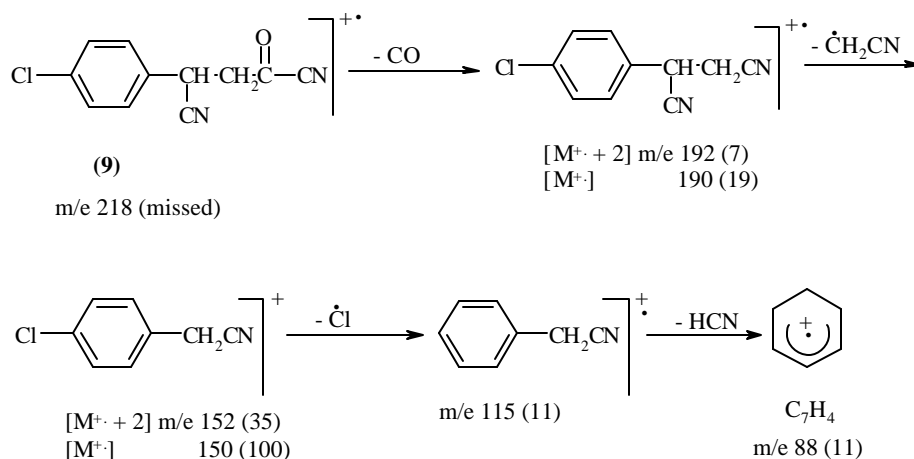
Scheme 3

However, treating (E, Z)-3-phenyl-5-(4-chlorophenylmethylene)-(3b)-, (E, Z)-3-allyl-5-(4-chlorophenylmethylene)-(3c)-and (E, Z)-3-isopropyl-5-(4-chlorophenylmethylene)-(3d)-1, 3-thiazolidin-2, 4-diones with potassium cyanide in boiling mixture of methanol and dioxane afforded 4-cyano-4-(4-chlorophenyl)-2-oxo-butryronitrile (9) as well as (E, Z)-5-(4-chlorophenylmethylene)-1, 3-thiazolidin-2, 4-dione (3f) and a water soluble adduct that upon treating its methanolic solution with chloroacetic acid gave ammonium chloroacetate 10 in case of 3c and 3d. Similar treatment of (E, Z)-3-allyl-5-(4-methoxyphenylmethylene)-1, 3-thiazolidin-2, 4-dione (3e) with potassium cyanide gave a mixture of (E, Z)-5-(4-methoxyphenylmethylene)-1, 3-thiazolidin-2, 4-dione (3g), but-3-eno-nitrile derivative (11) and a water soluble adduct that yielded compound (10) upon treating its methanolic solution with chloroacetic acid.



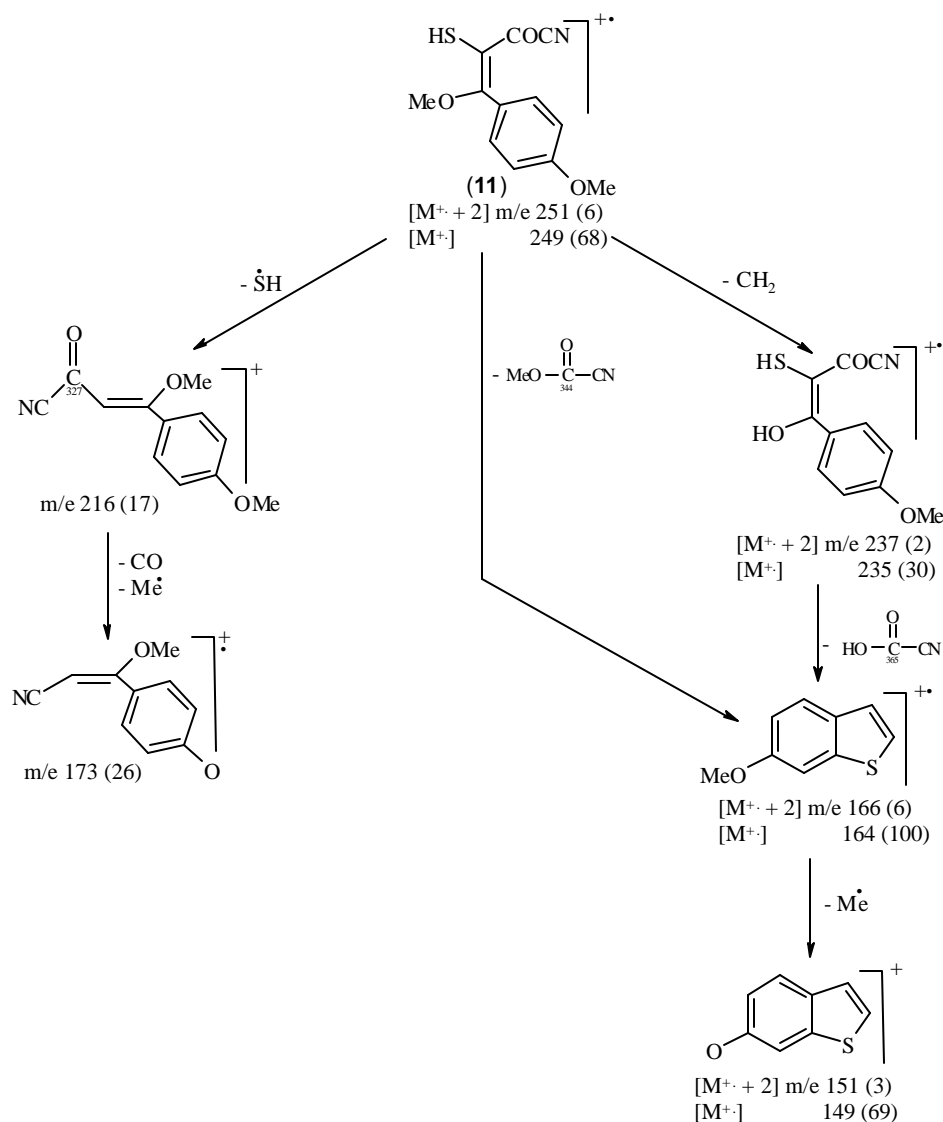
The structure of compounds 9 and 11 were substantiated from their analytical and spectral data. Their IR spectra exhibited stretching absorptions for CN and CO groups beside an additional absorption for SH group in case of compound 11.

The $^1\text{H-NMR}$ spectrum of compound 9 was consistent with the suggested structure as it showed from low to high field the signals of aromatic, methine and methylene protons. Its EI-MS spectrum didn't show the molecular ion peak, but it showed a peak at m/e 190 that corresponds to $(\text{M}^+ - \text{CO})$. The fragmentation pathway is represented in scheme 4.



Scheme 4

The $^1\text{H-NMR}$ spectrum of 11 revealed the existence of two closely spaced singlets for protons of two methoxy groups, an exchangeable singlet for SH proton as well as two doublet signals for aromatic protons. Moreover, the structure of 11 got further support from its EI-MS as it showed the molecular ion peak beside some of abundant peaks. The fragmentation pattern is shown in scheme 5.

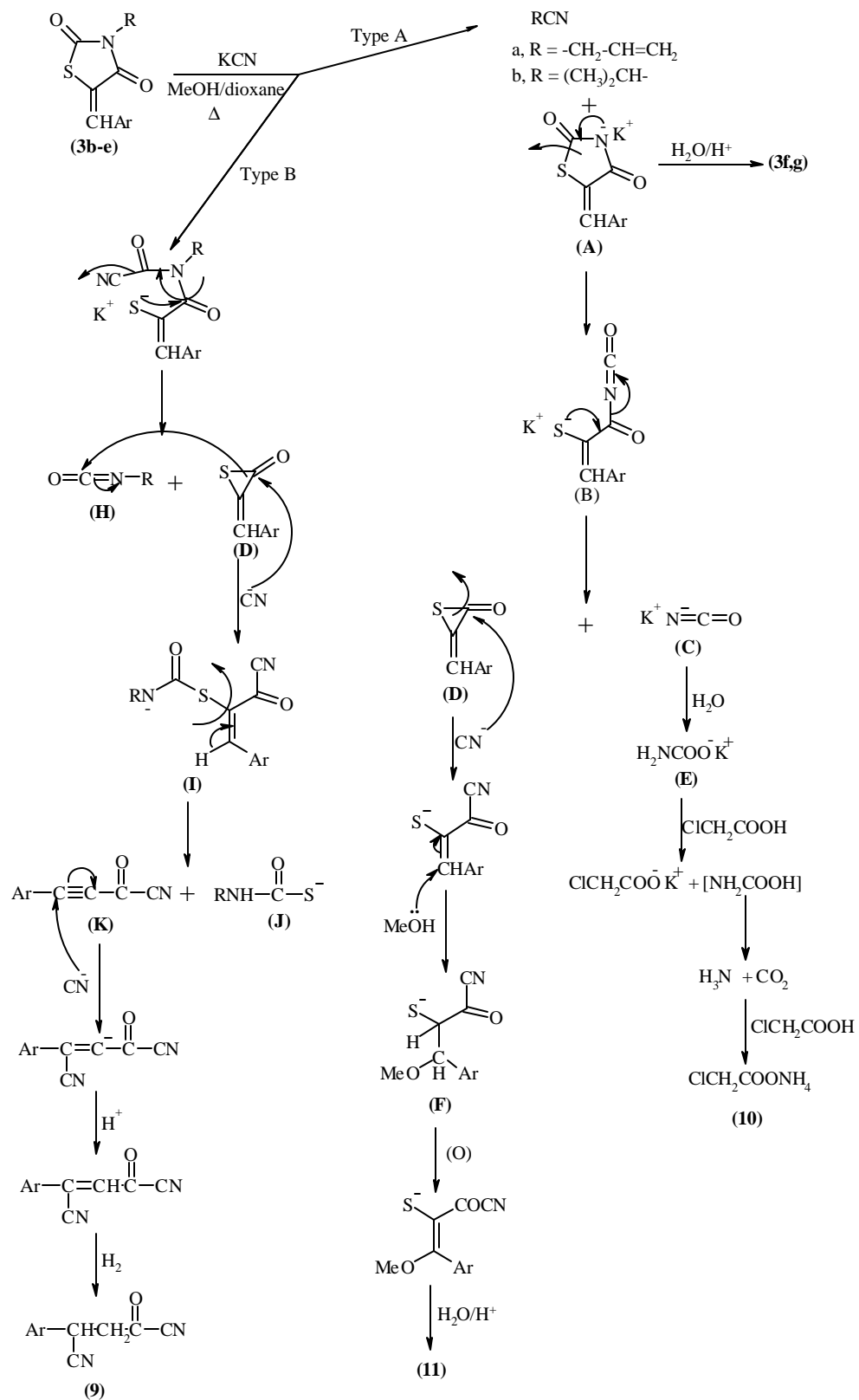


Scheme 5

The structures of compounds 3f and 3g were rigidly confirmed by m.p. comparison with those reported [7]. However, the structure of 10 was confirmed by mixture m.p. with authentic specimen.

The overall picture for the mode of action of cyanide ion on 3-aryl and 3-alkyl substituted-5-arylmethylene-1,3-thiazolidin-2,4-diones 3b-e is easily visualized as represented by type (A) and type (B) (Cf. Scheme 6). Type (A) involves an initial attack by cyanide ion at allyl or isopropyl group to afford the anion (A). Protonation of this anion yielded the adducts 3f and 3g. Thiazolidine ring opening of this anion at the 1,2-bond gave the thiolate anion (B), that underwent 3,4-bond cleavage to give the isocyanate (C) and the thirane (D). Addition of water to (C) gave the carbamate (E), which on treatment of its methanolic solution with chloroacetic acid afforded (10). A thirane ring opening through attack by CN^- ion at the 2-oxo group followed by addition of solvent molecule (MeOH) [9] at the β -carbon of the exocyclic double bond gave the methoxy adduct (F). Oxidation of the methoxy adduct (F) afforded (G) which upon protonation yielded (11).

Type (B) involves thiazolidine ring opening through successive cleavage at the 1,2-as well as the 3,4-bonds to give the isocyanate (H) and the thirane (D). Thirane ring opening through attack by cyanide ion at the 2-oxo group followed by reaction of the formed thiolate ion with the isocyanate (H) gave (I). Cleavage of (I) yielded the thiocarbamate (J) and the acetylenic ketone (K). Attack of cyanide ion at the β -acetylenic carbon of (K) followed by reduction afforded (9).



Scheme 6

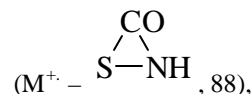
Experimental: All melting points are not corrected. IR spectra were measured on a Unicam SP1200 spectrometer as KBr discs. Unless otherwise stated the $^1\text{H-NMR}$ spectra were measured in CDCl_3 solution on Varian Gemini 200 MHz or Bruker ES 200 MHz instruments with chemical shift (δ) expressed in ppm downfield from Me_4Si . Mass spectra were recorded on Shimadzu GC-MS-QP 1000 Ex or Finnigan GCQ instruments operating at 70 eV. Column chromatography and TLC were run on Silica Gel Voein, activity III/30 mm according to Brockmann and Schodder and TLC aluminium sheets Silica Gel 60 F₂₅₄ (Merck).

Reactions of (1a, b) with (4a-c): A solution of (1a or 1b) (0.01 mole) and (4a-c) (0.01 mole) in 25 ml toluene in presence of ammonium acetate (0.03 mole) was refluxed for 15 h. The reaction mixture was cooled and then poured into cold water. The toluene layer was dried over anhydrous calcium chloride, concentrated and left to stand over night at room temperature. The precipitated solid was recrystallized from a proper solvent to give the adducts 5b, 6b in case of reactions of 1a with 4b, 4c. The adduct 5a was isolated from reaction of 1a with 4a and the residual oil was chromatographed over silica gel. Elution with petroleum ether (b.p. 40-60)/ether (4: 1 V/V) gave 6a. The precipitated solid in case of reaction of 1b with 4a was fractionally crystallized to give first 6c as yellow crystals (ethanol). The insoluble part in boiling ethanol was recrystallized from benzene to give 5a as white crystals.

2, 3, 5, 6-Tetraphenyl-1, 4-diazine (5a): 1.5 g (30%) white crystals (benzene), m.p. 241-243°C; IR: $\nu = 3080$ (aryl-H), 1615 (C = C and/or C = N), 760, 690 cm^{-1} ; $^1\text{H-NMR}$: $\delta = 7.31-7.68$ (m, 20, ArH); EI-MS m/z (%) 384 (M^+ , 77), 383 (68), 179 (14), 178 (base), 177 (20), 176 (35), 152 (20), 151 (14), 103 (13), 77 (10), 76 (13), 51 (11). Anal. Calcd. for $\text{C}_{28}\text{H}_{20}\text{N}_2$: C, 87.47; H, 5.24; N, 7.29. Found: C, 87.21; H, 5.49; N, 7.10%.

2, 6-Diphenyl-3, 5-di-(4-methoxyphenyl)-1, 4-diazine (5b): 1.1 g (25 %), white crystals (methanol-benzene), m.p. 190-192°C; IR: $\nu = 3020$ (aryl-H), 2920, 2830 (alkyl-H), 1610 (C = C and/or C = N), 835, 760, 700 cm^{-1} ; $^1\text{H-NMR}$: $\delta = 3.83$ (s, 6, 2OCH_3), 6.83-7.69 (m, 18, ArH); EI-MS m/z (%) 444 (M^+ , base), 443 (53), 208 (31), 193 (54), 165 (50), 164 (17), 163 (11), 139 (11), 104 (25). Anal. Calcd. for $\text{C}_{30}\text{H}_{24}\text{N}_2\text{O}_2$: C, 81.06; H, 5.44; N, 6.30. Found: C, 81.22; H, 5.11; N, 6.45%.

5-(1, 2-Diphenyl-2-hydroxy)ethylene-1, 3-thiazolidin-2, 4-dione (6a): 0.37 g (12%), yellow crystals (ethanol), m.p. 314-316; IR: $\nu = 3340, 3130$ (OH and/or NH), 3055 (aryl-H), 2930, 2860 (alkyl-H), 1740, 1690 (C = O), 765, 690 cm^{-1} ; $^1\text{H-NMR}$: $\delta = 4.02$ (δ 1, CH), 7.24-7.42 (m, 10, ArH), 10.01 (br.s, 1, OH exchangeable), 10.15 (br.s, 1, NH exchangeable); EI-MS m/z (%) 311 (M^+ , missed), 236



165 (16), 105 (63), 104 (base), 103 (16), 77 (51), 76 (12), 51 (35). Anal. Calcd. $\text{C}_{17}\text{H}_{13}\text{NO}_3\text{S}$: C, 65.58; H, 4.21; N, 4.49. Found: C, 65.41; H, 4.46; N, 4.19%.

5-(1-Phenyl-3-hydroxy)-but-2-en-1-ylene-1, 3-thiazolidin-2, 4-dione (6b): 0.39 g (15%), pale yellow crystals (ethanol), m.p. 140-142°C; IR: $\nu = 3314, 3160$ (OH and/or NH), 3060 (aryl-H), 2983, 2875 (alkyl-H), 1743, 1635 (C = O), 1595 (C = C), 641, 754 cm^{-1} ; EI-MS m/z (%) 261 (M^+ , missed), 161 ($\text{M}^+ - \text{HNCO-CH} = \text{C}(\text{OH})\text{CH}_3$, 38), 160 (88), 84 (base), 77 (33), 51 (29). Anal. Calcd. for $\text{C}_{13}\text{H}_{11}\text{NO}_3\text{S}$: C, 59.76; H, 4.24; N, 5.36. Found: C, 59.42; H, 4.39; N, 5.29%.

3-Phenyl-5-(1, 2-diphenyl-2-hydroxyethylene-1, 3-thiazolidin-2, 4-dione (6c): 0.77 g (20%), yellow crystals (ethanol), m.p. 138-140°C; IR: $\nu = 3380, 3210$ (OH and/or NH), 3070 (aryl-H), 2985, 2874 (alkyl-H), 1728, 1676 (C = O), 752, 692 cm^{-1} . Anal. Calcd. for $\text{C}_{23}\text{H}_{17}\text{NO}_3\text{S}$: C, 71.29; H, 4.42; N, 3.62. Found: C, 71.48; H, 4.23; N, 3.79%.

Reactions of 3-substituted-5-arylmethylene-1, 3-thiazolidin-2, 4-diones (3a-e) with sodium azide: A mixture of (3a-e) (0.01 mole) and sodium azide (0.03 mole) was refluxed in dimethylformamide (20 ml) for 20 h. The colour of the reaction mixture changed from yellow to brown then orange and yellow again. The precipitated solid during the reaction was filtered off, part of it was dissolved in water and then acidified with ice cold HCl, where no precipitate was obtained. This solid was identified as 8a and 8b. The reaction mixture was cooled, concentrated and then poured into ice cold water. The precipitated solid was recrystallized from a proper solvent to give (10-15%) of unreacted starting materials 3a-e. the filtrate was acidified with ice cold HCl. The solid obtained was fractionally crystallized to afford 3f and 3g in case of 3d and 3e (identical m.p with the reported [7]) and 7a-d, respectively.

E, Z-5-(4-Chlorophenylmethylene)-1, 3-thiazolidin-2, 4-dione (E, Z-3f): 0.6 g (10.0%); yellow crystals (ethanol-benzene), m.p. 224-226C, Lit. [7], m.p. 223-225.

E, Z-5-(4-Methoxyphenylmethylene)-1, 3-thiazolidin-2, 4-dione (E, Z-3g): 0.7 g (12%), yellow crystals (ethanol), m.p. 208-210C, Lit. [7], m.p. 212-214C.

1-Carboxy-2-phenyl-3-oxo-5-(4-methoxyphenyl)-2, 3-dihydropyrazole (7a): 1.55 g (50%), colourless crystals (ethanol-benzene), m.p. 152-154C; IR: $\nu = 3400, 3150$ (br.) (OH), 1665 (C = O), 1600 (C = C), 1550 (pyrazole ring), 830, 690 cm^{-1} ; $^1\text{H-NMR}$: $\delta = 3.77$ (s, OMe), 6.89-7.97 (m, 10, ArH + CH =), 9.1 (br.s, 1, OH exchangeable), EI-MS m/z (%) 310 (M^+ , missed), 294 ($\text{M}^+ - 16, 23$), 202 (26), 146 (15), 135 (24), 134 (19), 119 (25), 93 (base), 77 (20), 76 (15), 65 (16), 51 (17). Anal. Calcd. for $\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}_4$: C, 65.80; H, 4.55; N, 9.03. Found: C, 65.97; H, 4.35; N, 8.89%.

1-Carboxy-2-phenyl-3-oxo-5-(4-chlorophenyl)-2, 3-dihydropyrazole (7b): 1.73 g (55%), colourless crystals (xylene), m.p. 208-210C; IR: $\nu = 3389, 3196$ (br.) (OH), 1671 (C = O), 1601 (C = C), 1548 (pyrazole ring), 829, 747, 684 cm^{-1} ; $^1\text{H-NMR}$: $\delta = 7.37-7.98$ (m, 10, ArH + CH =), 8.92 (br.s, 1, OH exchangeable); EI-MS m/z (%) 314 (M^+ , missed), 300 ($\text{M}^+ + 2 - 16, 5$), 298 ($\text{M}^+ - 16, 15$), 206 (19), 139 (12), 123 (15), 93 (base) 77 (12), 65 (12), 51 (10). Anal. Calcd. for $\text{C}_{16}\text{H}_{11}\text{ClN}_2\text{O}_3$: C, 61.06; H, 3.52; N, 8.90. Found: C, 61.20; H, 3.39; N, 8.74%.

1-Carboxy-2-allyl-3-oxo-5-(4-chlorophenyl)-2, 3-dihydropyrazole (7c): 1.33 g (48%), metallic needles (ethanol), m.p. 130-132C; IR: $\nu = 3400, 3118$ (br.) (OH), 2980, 2906 (alkyl-H), 1668 (C = O), 1637, 1612 (C = C), 1559 (pyrazole ring), 824 cm^{-1} . $^1\text{H-NMR}$: $\delta = 4.08$ (m, 2, N- CH_2), 5.22 (m, 2, $\text{CH}_2 = \text{CH}$ -), 5.91 (m, 1, $\text{CH}_2 = \text{CH}$ -), 7.28-7.87 (m, 5, ArH + CH =), 13.05 (br.s, 1, OH exchangeable); EI-MS m/z (%) 278 (M^+ , missed), 264 ($\text{M}^+ + 2 - 16, 13$), 262 ($\text{M}^+ - 16, 37$), 247 (14), 208 (16), 206 (46), 138 (14), 123 (19), 114 (10), 57 (81), 56 (base). Anal. Calcd. for $\text{C}_{13}\text{H}_{11}\text{ClN}_2\text{O}_3$: C, 56.03; H, 3.98; N, 10.05. Found: C, 55.84; H, 4.12; N, 10.21%.

1-Carboxy-2-isopropyl-3-oxo-5-(4-chlorophenyl)-2, 3-dihydropyrazole (7d): 1.49 g (53%), colourless crystals (benzene-ethanol), m.p. 145-147C; IR: $\nu = 3406, 3104$ (br.) (OH), 3050 (aryl-H), 2948, 2899 (alkyl-H), 1669 (C = O), 1550 (pyrazole ring),

820 cm^{-1} ; $^1\text{H-NMR}$: $\delta = 1.26$ (d, 2 CH_3 , J = 6.5 Hz), 4.26 (m, 1, $\text{CH}(\text{CH}_3)_2$, J = 6.6 Hz), 7.25-7.79 (m, 5, ArH + CH =), 12.41 (br.s, 1, OH exchangeable); EI-MS m/z (%) 280 (M^+ , missed), 266 ($\text{M}^+ + 2 - 16, 5$), 264 ($\text{M}^+ - 16, 16$), 249 (16), 208 (14), 206 (43), 138 (13), 123 (19), 58 (base). Anal. Calcd. for $\text{C}_{13}\text{H}_{13}\text{ClN}_2\text{O}_3$: C, 55.62; H, 4.67; N, 9.98. Found: C, 55.41; H, 4.81; N, 9.66%.

Sodium 3-hydroxy-2-mercapto-p-chlorocinnamate (8a): 0.012 g (0.5%), white solid, m.p. >300C; IR: $\nu = 3491, 3426$ (OH), 2402, 2385 (w) (SH), 1637 (C = O), 881 cm^{-1} .

Sodium 3-hydroxy-2-mercapto-p-methoxycinnamate (8b): 0.011 g (0.6%), white solid, m.p. > 300C; IR: $\nu = 3589, 3419$ (w) (OH), 2496; 2362 (w) (SH), 1674 (C = O), 882 cm^{-1} .

Reactions of (3be) with potassium cyanide: A solution of (25 ml) dioxane containing (0.01 mole) 3b, 3c, 3d or 3e and (0.03 mole) potassium cyanide was heated to 90C for 25 min. During the reflux, 30 ml of methanol was added in five equal portions. The mixture was refluxed for 4 h. The precipitated solid during heating was filtered off and dissolved in water. Acidification with ice cold HCl was accompanied by effervescence without precipitation of solid. Treatment a methanolic solution of this solid with chloroacetic acid afforded 10. The reaction mixture was concentrated and left to stand at room temperature for 2 h. The precipitated solid was filtered off, dissolved in water and acidified with ice cold HCl to give a solid. Crystallization from (ethanol - benzene) afforded 3f in case of 3c and 3d, in a yield of 8%, m.p. 225-227C (identical with the reported [7]) and 3g as E/Z mixture in a ratio of 35:65 in case of 3e, yield of (10%), m.p. 208-210C (identical with the reported [7]). On leaving the mother liquor over night at room temperature, afforded compound 9 in case of 3b, 3c and 3d, while 11 was obtained in case of 3e.

Ammonium chloroacetate (10): 0.12 g (11%), white crystals (methanol), m.p. 137-139C (undepressed on admixture with an authentic sample prepared by passing ammonia gas over a methanolic solution of chloroacetic acid); IR: $\nu = 3401$ (NH), 2962, 2942, 2855 (alkyl-H), 1648 (C = O) cm^{-1} ; $^1\text{H-NMR}$ (DMSO- d_6): $\delta = 4.04$ (s, 2, CH_2), 4.83 (br.s, 4, NH_4 exchangeable); EI-MS m/z (%) 111 (M^+ , missed), 96 ($\text{M}^+ + 2 - \text{NH}_3, 1.4$), 94 ($\text{M}^+ - \text{NH}_3, 4.2$), 79 ($\text{CICH}_2\text{-C}^+\text{O}^+, 1.3$), 78 ($\text{CICH} = \text{C} = \text{O}, 0.5$), 77 ($\text{CICH}_2\text{C}^+\text{O}^+, 4.3$), 76 ($\text{CICH} = \text{C} = \text{O}, 1$), 58 ($\text{M}^+ - \text{NH}_3\text{-HCl}, 1$), 50 ($\text{M}^+ - \text{NH}_3 - \text{CO}_2$, base).

4-Cyano-4-chlorophenyl-2-oxo-butylonitrile (9): 0.87-1.31 g (40-60%), creamy crystals (ethanol), m.p. 87-89°C; IR: $\nu = 3050$ (aryl-H), 2973, 2945 (alkyl-H), 2247 (CN), 1657 (C = O), 825 cm^{-1} ; $^1\text{H-NMR}$: $\delta = 2.97$ (m, 2, CH_2 , $J = 6.4$ Hz), 4.15 (t, 1, CH, $J = 6.8$ Hz), 7.37 (d, 2, H_a , H_a' , $J_o = 6.8$ Hz), 7.46 (d, 2, H_b , H_b' , $J_o = 6.8$ Hz). EI-MS m/z (%) 218 (M^+ , missed), 192 ($\text{M}^+ + 2 - \text{CO}$, 7), 190 ($\text{M}^+ - \text{CO}$, 19), 152 ($\text{M}^+ + 2 - \text{CH}_2\text{COCN}$, 36), 150 ($\text{M}^+ - \text{CH}_2\text{COCN}$, base), 115 (11), 88 (11), 75 (22), 74 (14), 63 (20), 62 (13), 61 (11), 51 (21), 50 (34). Anal. Calcd. for $\text{C}_{11}\text{H}_7\text{ClN}_2\text{O}$: C, 60.43; H, 3.23; N, 12.81. Found: C, 60.25; H, 3.31; N, 12.56%.

3-Mercapto-4-methoxy-4-(methoxyphenyl)-2-oxo-but-3-enonitrile (11): 1.2 g (48%), pale brown crystals (ethanol), m.p. 279-281; IR: $\nu = 3001$ (aryl-H), 2929-2840 (alkyl-H), 2423 (SH), 2056 (CN), 1673 (C = O), 1607 (C = C), 817 cm^{-1} ; $^1\text{H-NMR}$ (DMSO-d_6): $\delta = 3.76, 3.77$ (two singlets, 2OCH_3), 2.49 (br.s, 1, SH exchangeable), 7.01 (d, 2, H_b , H_b' , $J_o = 8.8$ Hz), 7.47 (d, 2, H_a , H_a' , $J_o = 8.6$ Hz); EI-MS m/z (%) 251 ($\text{M}^+ + 2$, 6), 249 (M^+ , 68), 237 (2), 235 (30), 216 (17), 191 (13), 174 (18), 173 (26), 165 (11), 164 (base), 163 (49), 149 (69), 148 (18), 145 (25), 121 (22), 120 (22), 119 (12), 94 (12), 89 (14), 82 (10), 77 (25), 69 (13),

63 (14), 62 (13), 51 (17), 50 (11). Anal. Calcd. for $\text{C}_{12}\text{H}_{11}\text{NO}_3\text{S}$: C, 57.82; H, 4.45; N, 5.62. Found: C, 57.52; H, 4.62; N, 5.74%.

REFERENCES

1. Omar, M.T., M.M. Habashy, A.M. Youssef and F.A. Sherif, 1989. *J. Prakt. Chemie*, 331: 393.
2. Omar, M.T. and F.A. Sherif, 1981. *Synthesis*, No. 9: 742.
3. Raouf, A.R.A., M.T. Omar and M.M. El-Attal, 1975. *Acta. Chimica. Sci. (Hung.)*, 87: 187.
4. Raouf, A.R.A., M.T. Omar and M.M. El-Attal, 1975. *Acta. Chimica. Sci. (Hung.)*, 83: 367.
5. Omar, M.T., M.M. Habashy and A. El-Khamry, 1980. *Aust. J. Chem.*, 33: 619.
6. Campaigne, E. and R.E. Cline, 1956. *J. Org. Chem.*, 21: 32.
7. Lo, C.P., E.Y. Shorpsshire and W.J. Croxall, 1953. *J. Am. Chem. Soc.*, 75: 4845.
8. Elguero, J., C. Marzin, A.R. Katritzky and P. Linda, *The Tautomerism of Heterocycles*, Academic Press, New York, 1976.
9. Papa, D., E. Schwenk, F. Villiani and E. Klingsberg, 1948. *J. Am. Chem. Soc.*, 70: 3555.