Behavior of Acetylenic Ketones and Esters towards Aroylisothiocyanates in Polar Solvent (Part I)

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Comportamiento de cetonas y ésteres acetilénicos frente a isotiocianatos de aroílo en disolventes polares (Parte I)

Comportament de cetones i esters acetilènics envers isotiocianats d'aroïl en solvents polars (Part I)

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RESUMEN

Las reacciones de los aroílisotiocianatos **2a,b** con las cetonas acetilénicas **1a-c** dan una mezcla de tiocianatoprop-2-en-1-onas **3a-c**, (***E,Z***)-3,3'-tiodi(1-aril-3-fenilprop-2-en-1-onas) **4a-c**, 4-metoxibenzoíltiourea (6), 3-(4-metoxibenzamido)-1,3-difenilprop-2-en-1-ona (7a) y 2-fenilacetamida (8). El tratamiento de 2a,b con los ésteres acetilénicos **1d,e** rinde una mezcla de (***Z,Z***)-3,3'-tiodiacrilatos **5a,b**, la tiourea **6**, 3-(2-fenilacetamido)-3-fenilprop-2-enoato (7b), y 8. Al hacer reaccionar 1f con 2a se obtiene el derivado de tetrahidropirimidina 9 y el compuesto 6. Finalmente, con **2b** se obtiene **8**.

Palabras clave: aroílisotiocianatos, cetonas acetilénicas, ésteres acetilénicos, tiocianatoprop-2-en-1-onas, tiodiacrilatos, aroíltiourea, tiodiprop-2-en-1-onas, tetrahidropirimidina.

SUMMARY

Reactions of aroylisothiocyanates **2a,b** with acetylenic ketones **1a-c** gave a mixture of thiocyanatoprop-2-en-1-ones **3a-c**, (***E,Z***)-3,3'-thiodi(1-aryl-3-phenylprop-2-en-1-ones) **4a-c**, 4-methoxybenzoylthiourea (**6**), 3-(4-methoxybenzamido)-1,3-diphenylprop-2-en-1-one (7a) and 2-phenylacetamide **(8)**. Treatment of **2a,b** with acetylenic esters **1d,e** afforded a mixture of (***Z,Z***)-3,3'-thiodiacrylates **5a,b**, the thiourea **6**, 3-(2-phenylacetamido)-3-phenylprop-2-enoate (7b) and **8**. Reacting **1f** with **2a** yielded tetrahydropyrimidine derivatives **9** and **6**. On the other hand, with **2b** yielded **8**.

Keywords: aroylisothiocyanates, acetylenic ketones, acetylenic esters, thiocyanatoprop-2-en-1-ones, thiodiacrylates, aroylthiourea, thiodiprop-2-en-1-ones, tetrahydropyrimidine.

RESUM

Les reaccions dels aroïlisotiocianats **2a,b** amb les cetones acetilèniques **1a-c** donen una barreja de tiocianatoprop-2-en-1-ones **3a-c**, (***E,Z***)-3,3'-tiodi(1-aril-3-fenilprop-2-en-1-ones) **4a-c**, 4-metoxibenzoïltiourea (**6**), 3-(4-metoxibenzamido)-1,3-difenilprop-2-en-1-ona (**7a**) i 2-fenilacetamida (**8**). El tractament de 2a,b amb els esters acetilènics **1d,e** rendeix una mescla de (***Z,Z***)-3,3'-tiodiacrilats **5a,b**, la tiourea **6**, 3-(2-fenilacetamido)-3-fenilprop-2-enoat (**7b**), i **8**. En fer reaccionar **1f** amb **2a** s'obté el derivat de tetrahidropirimidina **9** i el compost **6**. Finalment, amb **2b** s'obté **8**.

Mots clau: aroïlisotiocianats, cetones acetilèniques, esters acetilènics, tiocianatoprop-2-en-1-ones, tiodiacrilats, aroïltiourea, tiodiprop-2-en-1-ones, tetrahidropirimidina.

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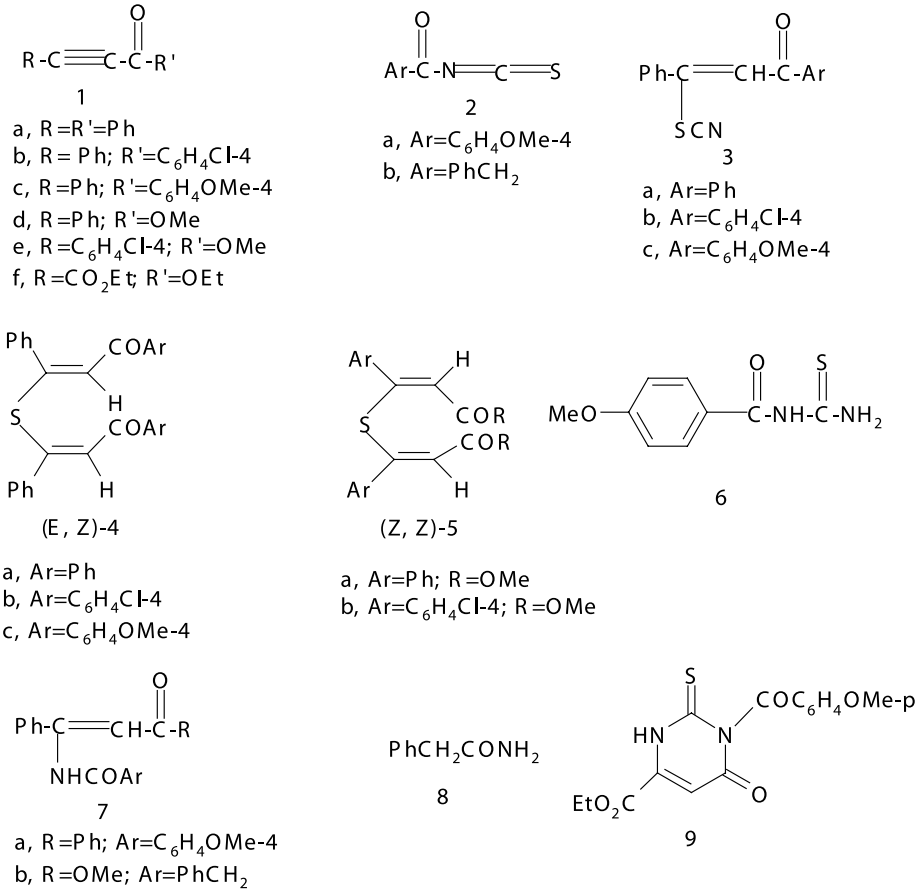
The cycloaddition reactions of isothiocyanates with acetylenic compounds have received extremely a little attention. Aroyl isothiocyanates condense with acetylenic amides to give 1,3-thiazolidin-4-ones[1] and 1,4-thiazin-3-ones[2]. It appeared that the intramolecular nucleophilic addition of sulfur atom of isothiocyanates had actually occurred at α-carbon rather than β-carbon of acetylenic bond. There are no reports dealt with reactions of aryl and aroyl isothiocyanates with acetylenic ketones and esters. In the present work we aimed to prepare some heterocyclic oxazinthiones[3-7] of anticipated biological activities through reactions of aroyl isothiocyanates with acetylenic ketones and esters via [4+2] cycloadditions. Unfortunately, we get instead mainly unexpected open chain adducts that reflects unsuitability of acetone as a medium for the cycloaddition reactions. Utilization of non polar solvent as a medium for these reactions is under investigation now.

Treatment of acetylenic ketones **1a-c** with aroyl isothiocyanates **2a,b** in refluxing dry acetone afforded a mixture of 3-thiocyanato prop-2-en-1-one derivatives **3a-c** (major) and (***E,Z***)-3,3'-thiodi(1-aryl-3-phenylprop-2-en-1-ones) **4a-c** as well as 4-methoxybenzoyl thiourea **6** from reaction **1c** with **2a**, 3- (4-methoxybenzamido)-1,3-diphenylprop-2-en-1-one **(7a)** from reaction **1a** with **2a** and 2-phenylacetamide (**8)** in case of reaction **1a** with **2b**, respectively (in minor amounts) (cf. Scheme 1). Similar treatment of aroyl isothiocyanates **2a,b** with acetylenic esters **1d,e** yielded (***Z,Z***)-3,3'-thiodiacrylates **5a**,**b** as well as 4-methoxybenzoylthiourea **6** in case of reaction with **2a** in addition to methyl 3-(2-phenylacetamido)-3-phenylprop-2-enoate **7b**, **8** in case of reaction with **2b**. Reaction of **1f** with **2a** furnished tetrahydro pyrimidine derivative **9** and **6**; on the other hand, its reaction with **2b** gave compound **8** beside unidentifiable high melting point compound (cf. Scheme 1).

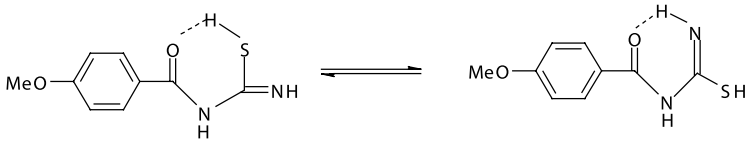
The structures of compounds **3-9** were deduced from their micro analytical and spectral data. The infrared spectra of compounds **3-5, 7a** show $\upsilon_{C=O}$ consistent with carbonyl groups. The spectrum of **3** exhibits υ_{SCN}. The spectra of compounds **6-9** reveal $\upsilon_{C=O}$ amide, υ_{NH} as well as $\upsilon_{C=O}$ ester for compound **9** in addition to $\upsilon_{C=S}$ absorption in case of compounds **6** and **9**. The n. m. r. spectrum is in accord with the proposed structure of **3**. Configurationally assignments to **4** and **5** were based on their n. m. r. spectra. The spectrum of **4c** shows multiplet signals in the region δ 6.67-8.10 and two singlets at δ 3.89 and 3.79 (signal ratio 20: 3: 3), the olefinic proton signals overlapping with those of aromatic protons. The appearance of two signals due to methoxy protons indicates that the anisoyl groups are in different environments and is consistent with an (***E***, ***Z***)-configuration of **4c**. The appearance of one singlet signal for methoxy protons (δ 3.76, 6 protons) in the isomer **5a** is a good evidence for existence of methoxy protons in identical environments. So the configuration of **5a** must be (***E,E***) or (***Z,Z***). The (***Z,Z***)-configuration was assigned on the basis of a comparison of its n. m. r. spectrum with those of (***E***)- and (***Z***)-3-p-bromophenylthio-1,3-diphenylprop-2-en-1-ones[8] obtained by the base catalyzed addition of *p*-bromo benzenethiol to benzoylphenyl acetylene. The olefinic proton in the (***E***)-isomer appears as a singlet at δ 6.46, whereas it is more deshielded in its (***Z***)-isomer and its signal overlaps with those of the aromatic protons. The assignment of configuration to the (***E***) - and (***Z***) - isomer is based on the deshielding effect caused by a phenyl group on a β-cis olefinic proton relative to a β-trans proton[9], a



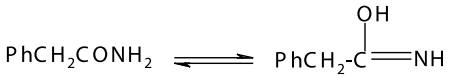
Scheme 1

feature which has tested previously and found characteristic of a number of styrene derivatives[10].

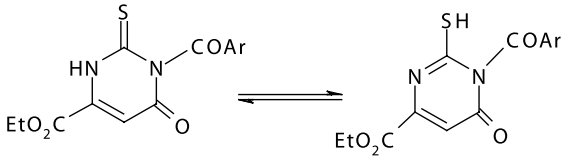
The n. m. r. spectrum shed further light on the assigned structure to compound **6** as it displayed singlet signal due to methoxy protons at δ 3.8, multiplet signals equivalent to four aromatic protons in the region 7.01-7.98 ppm as well as three broad singlet signals in the down field region at δ 9.51, 9.91 and 11.07 ppm. The appearance of signals due to NH and NH_2 protons in the down field region as three rather than two broad singlets is a good proof for existence of compound **6** in chloroform as its chelated tautomers shown.



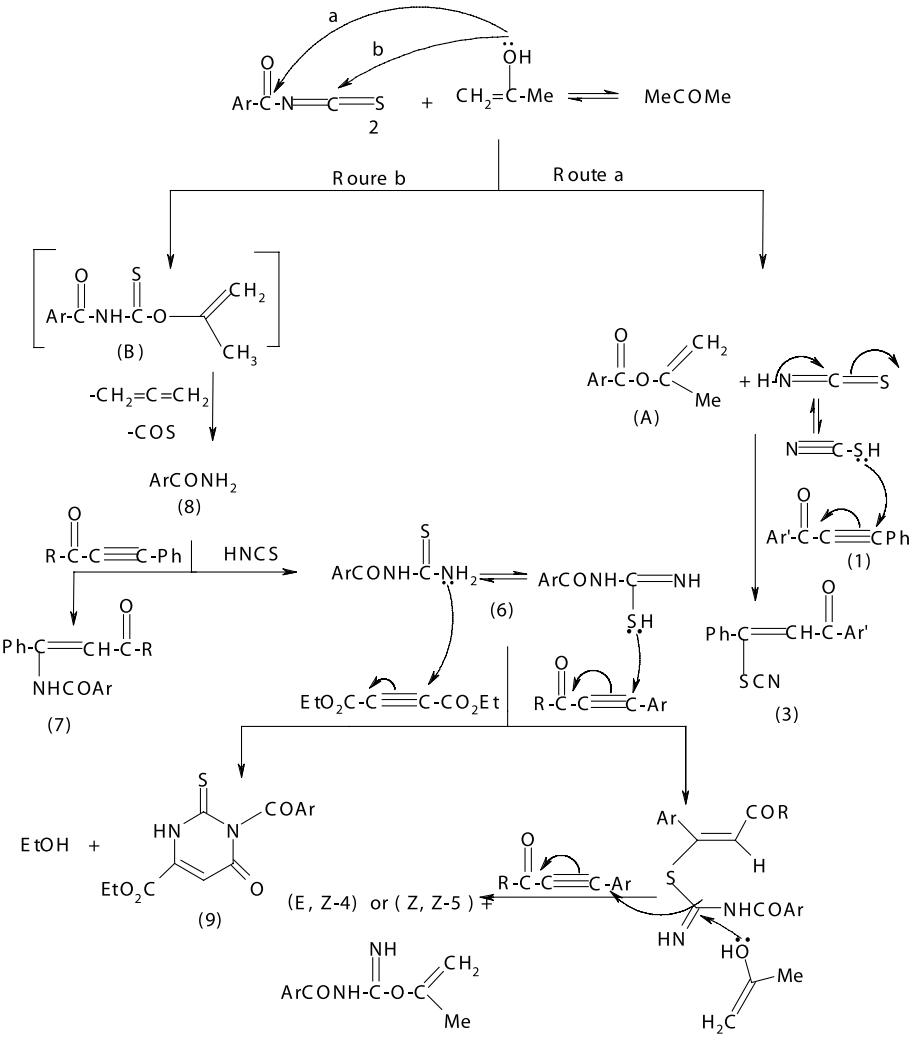
Inspection of the n. m. r. spectrum of compound **8** revealed the existence of a singlet signal at δ 3.59 correlated with CH_2, multiplet signals in the region 7.25-7.38 ppm owing to five aromatic protons, one broad singlet signal at δ 1.81 ppm equivalent to one proton and two broad singlet signals at δ 5.44, 5.77 ppm, the first one corresponds to two protons and the second equivalent to one proton. The appearance of the signals corresponding to NH_2 protons as three broad singlet signals ; two equivalent to two protons and the third one integrating two protons is a good support for the existence of compound **8** as a mixture of amino-imino tautomer in a ratio of 1 : 1 as shown.



The structure assigned to compound **9** was gleaned from its n. m. r. spectrum. The appearance of two broad singlets each integrated one proton; one up field and the other in the down field region is in good agreement with its existence as a mixture of two tautomeric forms in a ratio of 1 : 1 (as shown).



Further support for the assigned structures to compounds **3-9** is found in their mass spectra that revealed the molecular ions and other abundant peaks in accord with their proposed structures.



Scheme 2

The formation of compounds **3-9** is visualized to proceed through two routes (cf. scheme 2). **Route a**: involves nucleophilic attack of the acetone enol-tautomer at the aroyl function of isothiocyanates **2** to afford the intermediate ester (**A**) (not isolated) and isothiocyanic acid. Reaction of isothiocyanic acid formed with the acetylenic ketones **1** gave the thiocyanatoprop-2-en-1-one derivatives [11] **3**. **Route b**: comprises the attack by acetone enol-tautomer at isothiocyanato function of **2** to give the thiocarbamic ester (B) that underwent cleavage to afford the amide **8**, allene and carbonyl sulfide. Reaction of amide **8** with acetylenic ketone **1a** or ester **1d** gave the adduct **7**. On the other hand, its reaction with isothiocyanic acid (isolated from route a) yielded the aroylthiourea **6**. Compound **6** attacks the acetylenic ketones or esters **1** by the sulfur atom [12], followed by a rapid isomerization of the formed intermediate 1:1 adduct (not isolated) before its reaction with a second molecule of acetylenic ketone. Such an isomerization is favored since it facilitates the attack on the second molecule of the acetylenic ketone by minimizing the steric interaction and may explain the preponderance of the (***E, Z***)-isomer [8, 11-13] in case of acetylenic ketones. On the other hand the attack of **6** by its terminal amino group at the β-acetylenic carbon of **1f** followed by cyclization gave pyrimidine derivative **9**.

CONCLUSION

Aroyl isothiocyanates are much more reactive toward acetone (polar solvent) than acetylenic ketones and esters; however, we are interested in our future work in using non polar solvent in these reactions on the hope to synthesize the aimed cycloaddition products.

EXPERIMENTAL

Melting points were determined in open capillary tubes on a Griffin melting point apparatus and are uncorrected. The elemental analyses were carried out at the Micro Analytical Unit, Faculty of Science, Cairo University by using Perkin-Elemer 2400 CHN elemental analyzer. The IR spectra were measured on a unicam SP 1200 or FTIR Mattson (infinity series) spectrometers as KBr discs. Unless otherwise stated the ^{1}HNMR spectra were measured in DMSO-d_6 solution on Varian Gemini 200 MHz instrument with chemical shift (δ) expressed in ppm downfield from Me_4Si. Mass spectra were recorded on Shimadzu GC-MS-QP 1000 EX operating at 70 ev. Column chromatography and TLC were runned on silica Gel Voeim 111 / 30 mm according to Brockmann and Schodder and TLC aluminum sheets silica Gel 60 F_{254} (Merck, Fedral Rupublic Germany). 'Light petroleum' refers to the fraction b.p. 60-80 °C, unless otherwise specified. Acetylenic ketones[14] and esters[15] (**1**) were prepared according to literature methods.

(A) General procedure for synthesis of *p*-anisoyl or phenylacetyl isothiocyanate (2a or 2b). To a solution of *p*-anisoyl chloride or phenylacetyl chloride (5 mmol) in dry acetone (20 ml), solid ammonium thiocyanate (7 mmol) was added. The reaction mixture was stirred for half an hour at room temperature [16,17]. The precipitated ammonium chloride was filtered off to give a clear yellow solution of aroyl isothiocyanate **2a** or **2b**.

(B) General procedure for reaction of *p*-anisoyl isothiocyanate (2a) with acetylenic ketones or esters 1a-f. A solution of isothiocyanate **2a** (5mmol) in dry acetone (20 ml) was added portion wise to a solution of an equivalent amount of each of acetylenic ketones or esters **1a-f** in dry acetone (10 ml) and the whole mixture was refluxed on boiling water bath for 5-6 h. The reaction mixture was left to evaporate at room temperature and the residual oil was triturated with methanol to give either oil or a solid which was chromatographed or crystallized from the appropriate solvent.

The oil product obtained upon treating **1a** with **2a** was chromatographed over silica gel. Elution with a mixture of light petroleum / diethyl ether (9:1 v/v) gave **3a** as yellow lemon crystals. Successive elution with a mixture of light petroleum / diethyl ether (8:2 v/v) gave **4a** as yellow crystals. Elution with diethyl ether afforded **7a** as yellow crystals. The solid obtained from reaction of **1b** with **2a** after evaporation of acetone was recrystallised from ethanol to give **3b** as yellow crystals. The mother liquor leaves a solid which was recrystallised from benzene to afford **4b** as golden yellow crystals. The residual oil left after evaporation of acetone in case of reaction **1c** with **2a** was triturated with methanol to give a solid which was recrystallised from ethanol as yellow lemon crystals **6**. The methanol mother liquor was evaporated and chromatographed over silica gel. Elution with a mixture of light petroleum / ether (9:2 v/v) gave **3c** as yellow needles. Further elution with a mixture of light petroleum / diethyl ether (1:1 v/v) afforded **4c**.

In case of reaction **1d** or **e** with **2a**: The solid obtained after trituration with methanol was recrystallised from ethanol to give unreacted **1e**. On leaving the mother liquor to stand at room temperature it gave **6** in both cases. The residual oil obtained after evaporation of methanol was chromatographed over silica gel. Elution with a mixture of light petroleum / diethyl ether (2:1 v/v) gave **5a**; while **5b** was isolated on elution with the same mixture (1:1 v/v). On the other hand, reaction of **1f** with **2a** gave a solid; precipitated during reflux which was filtered off and recrystallised from dioxane to give **9**. Leaving the mother liquor to evaporate at room temperature, afforded a solid product which was recrystallised from ethanol to give **6**.

(D) General procedure for reaction of phenylacetyl isothiocyanate (2b) with acetylenic ketones and esters 1a-f. The same quantities and steps were carried out as in the previous procedure. Acetone was evaporated and the residual oils left in case of reactions **1a**, **1e**, and **1f** with **2b** were chromatographed over silica gel. In case of reaction **1a** with **2b**: elution with a mixture of light petroleum / diethyl ether (6:1 v/v) gave **3a**. Compound **4a** was obtained by elution with a mixture of light petroleum / diethyl ether (1:1 v/v). Further elution with diethyl ether yielded **8**. The oil product obtained from reaction of **1e** with **2b** was eluted with a mixture of light petroleum / diethyl ether (5:1 v/v) to produce **5b**. Successive elution with diethyl ether gave **8**. On other hand**,** the oily product of reaction **1f** with **2b** was eluted with a mixture of diethyl ether / ethyl acetate (1:1 v/v) to afford **8**. The unidentified substance was precipitated during reflux.

The reaction mixtures of **1b**-**d** with isothiocyanate **2b** were left to stand at room temperature to give solid products.

Crystallization from proper solvents gave **3b, 3c** and **7b**, respectively. On leaving the mother liquors at room temperature, solids separated were crystallized from suitable solvents to afford **4b, 4c** and **5a** respectively.

1,3-Diphenyl-3-thiocyanatoprop-2-en-1-one (3a), (45-58 %), yellow lemon crystals (light petroleum / benzene), m. p. 91-93 °C (lit.[11] m. p. 95-96 °C); IR: 3060 (aryl-H), 2150 (SC≡N), 1633 (C=O), 1589, 1552 (C=C), 752, 692 Cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 7.41 (s, 1, CH=), 7.31-8.04) (m, 10, ArH). MS m/z (%): 267 (M^++2, 1.4), 265 (M^+, 25), 239 (12), 238 (47), 105 (PhCO, 100), 102 (8), 77 (Ph, 52), 51 (20). Anal. Calcd for $C_{16}H_{11}NOS$: C, 72.43; H, 4.18; N, 5.28 %. Found: C, 72.50; H, 3.99; N, 5.07 %.

1-(4-Chlorophenyl)-3-phenyl-3-thiocyanatoprop-2-en-1-one (3b), (60-63 %), yellow crystals (ethanol), m.p.115-117°C (lit.[11] m.p. 119-120 °C); IR: 3086 (aryl-H), 2150 (SC≡N), 1635 (C=O), 1585, 1537 (C=C), 821, 758,694 Cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 7.38 (s, 1, CH=), 7.35-7.97 (m, 9, ArH). MS m/z (%): 301 (M^++2, 7), 300 (12), 299, (M^+, 16), 298 (23), 274 (14), 272 (23), 141 (37), 139 (COC_6H_4Cl-p,100), 113 (22), 111 (C_6H_4Cl-p, 55), 105 (14), 102 (14), 86 (13), 75 (25), 51 (21), 50 (11). Anal. Calcd for $C_{16}H_{10}ClNOS$: C, 64.11; H, 3.36; N, 4.67 %. Found: C, 64.22; H, 3.27; N, 4.75 %.

1-(4-Methoxyphenyl)-3-phenyl-3-thiocyanatoprop-2-en-1-one (3c), (49-53 %), yellow needles (light petroleum / benzene), m. p. 88-90 °C (lit.[11] m. p. 97-98 °C); IR: 3051 (aryl-H), 2968, 2929, 2835 (alkyl-H), 2152 (SC≡N), 1642 (C=O), 1597, 1545 (C=C), 820, 766, 696 Cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.90 (s, 3, OCH_3), 6.99 (d, 2, ArH, J_o= 8.88 Hz), 7.37 (s, 1, CH=), 7.47-7.55 (m, 5, ArH), 8.00 (d, 2, ArH, J_o= 8.86 Hz). MS m/z (%): 297 (M^++2, 2.4), 295 (M^+, 32), 294 (45), 268 (23), 135 ($COC_6H_4OCH_3$-p, 100), 107 ($C_6H_4OCH_3$-p, 13), 105 (10), 92 (26),77 (39), 64 (16), 63 (12). Anal. Calcd for $C_{17}H_{13}NO_2S$: C, 69.13; H,4.44; N, 4.74 %. Found: C, 69.24; H, 4.28; N, 4.59 %.

(E,Z)-3,3'-Thiodi(1,3-diphenylprop-2-en-1-one) (4a), (22-27 %), yellow needles (light petroleum b.p. 80-100), m. p. 135-137 °C (lit.[8,11] m. p. 139, 137-139 °C); IR: 1650 (C=O), 1610, 1550 Cm^{-1} (C=C). ^{1}H-NMR ($CDCl_3$) δ: 6.84 (s, 1, CH=), 7.43 (s, 1, CH=), 7.33-7.89 (m, 20, ArH). Anal. Calcd for $C_{30}H_{22}O_2S$: C, 80.69; H, 4.97 %. Found: C, 80.81; H, 4.86 %.

(E,Z)-3,3'-Thiodi(1-[4-chlorophenyl]-3-phenylprop-2-en-1-one (4 b), (23-25 %), golden yellow crystals (benzene), m. p. 163-165 °C (lit.[8,11] m. p. 160, 159-160 °C); IR: 1631 (C=O), 1585, 1541 (C=C), 823, 760, 694 Cm^{-1}. ^{1}H-NMR (DMSO-d_6) δ: 6.92 (s, 1 CH=), 6.80-8.21 (m, 18, ArH), 7.74 (s, 1, CH=). MS m/z (%): 515 (M^+, 3), 512 (8), 374 (M^+-*p*-ClC_6H_4CHO, 12), 276 (16), 275 (40), 274 (41)273 (M^+-PhC=CHCOC_6H_4Cl-p, 100), 239 (13), 141 (18), 139 (COC_6H_4Cl-p, 65),121 (15), 113 (15), 111 (C_6H_4Cl-p, 43), 91 (10), 77 (12), 75 (19), 51 (18). Anal. calcd for $C_{30}H_{20}Cl_2O_2S$: C, 69.90; H, 3.91 %. Found: C, 69.79; H, 4.03 %.

(E,Z)-3,3'-Thiodi(1-[4-methoxyphenyl]-3-phenylprop-2-en-1-one*)* (4c), (18-23 %), yello**w** crystals (ethanol**),** m. p. 151-153 °C (lit.[8,11] m. p. 150-152, 152 °C); IR: 1665 (C=O), 1604, 1555 Cm^{-1} (C=C)**.** ^{1}H**-**NMR ($CDCl_3$) δ: 3.79, 3.89 (two singlets, 2 OCH_3 protons), 6.67-8.10 (m, 18 ArH+2 CH=). Anal. Calcd for $C_{32}H_{26}O_4S$: C, 75,87; H, 5.17 %. Found: C, 75.72; H, 5.06 %.

(Z,Z)-Thiodi (methyl 3-phenylprop-2-enoate) (5a), (60-63 %), yellow crystals (ethanol), m. p. 156-158 °C; IR: 3071, 3036 (aryl-H), 2947, 2871 (alkyl-H), 1726 (C=O), 1585, 1535 (C=C), 766, 702 Cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.76 (s, 6, 2 OCH_3), 7.38-7.53 (m, 10 ArH+2 CH=). MS m/z (%): 356 (M^++2, 1), 354 (M^+, 8), 353 (25), 352 (95), 322 (26), 321 (100), 234 (15), 121 (17), 77 (11). Anal. Calcd for $C_{20}H_{18}O_4S$: C, 67,78; H, 5.12 %. Found: C, 67.86; H, 5.25 %.

(Z, Z)-3, 3'-Thiodi (methyl 3-[4-chlorophenyl]prop-2-enoate) (5b), (51-56 %), yellow crystals (methanol), m. p. 149-151 °C; IR: 3071 (aryl-H), 2945 (alkyl-H), 1722 (C=O), 1539, (C=C), 829 Cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.84 (s, 6, 2 OCH_3), 7.36-7.46 (m, 8 ArH+2 CH=). MS m/z (%): 425 (M^++2, 5), 424 (14), 423 (M^+, 12), 422 (64), 421 (24),420 (100), 419 (10), 393 (13), 392 (17), 391 (60), 390 (22), 389 (83), 388 (17), 298 (10), 139 (COC_6H_4Cl-p, 15), 111 (C_6H_4Cl-p, 11). Anal. Calcd for $C_{20}H_{16}Cl_2O_4S$: C, 56.75; H, 3.81 %. Found: C, 56.61; H, 3.93 %.

4-Methoxybenzoylthiourea (6), (9-15 %), yellow lemon crystals (ethanol), m. p. 202-204 °C; IR: 3348, 3238, 3176 (NH), 3083 (aryl-H), 2998, 2922, 2833 (alkyl-H), 1685 (C=O), 1560, 1549 (C=C), 1174 (C=S), 850 Cm^{-1}. ^{1}H-NMR (DMSO-d_6) δ: 3.84 (s, 3, OCH_3), 7.03 (d, 2, ArH, J_o= 8.8 Hz), 7.96 (d, 2, ArH, J_o= 9 Hz), 9.51 (br.s, 1, SH exchangeable), 9.91 (br.s, 1, NH exchangeable), 11.07 (br.s, 1, NH exchangeable). Anal. calcd for $C_9H_{10}N_2O_2S$: C,51.41; H, 4.79; N, 13.32 %. Found: C, 51.53; H, 4.65; N, 13.49 %.

3-(4-Methoxybenzamido)-1,3-diphenylprop-2-en-1-one (7a), (11 %), yellow crystals (ethanol), m. p. 214-216 °C; IR: 3367, 3334, 3207 (NH), 3028 (aryl-H), 2986, 2929, 2841 (alkyl-H), 1697, 1660 (C=O), 1604, 1585 (C=C), 841, 766, 694 Cm^{-1}. MS m/z (%): 357 (M^+, 0.1), 329 (M^+ -CO, 13), 194 (M^+ -COC_6H_4OMe-p, 13), 135 (COC_6H_4OMe-p, 100), 107 (C_6H_4OMe-p, 4), 92 (9), 77 (16), 63 (13), 51 (10). Anal. Calcd for $C_{23}H_{19}NO_3$: C, 77.29; H, 5.36; N, 3.92 %. Found; C, 77.19; H, 5.49; N, 4.03 %.

Methyl 3-(2-phenylacetamido)-3-phenylprop-2-enoate (7b), (19 %), pale yellow crystals (light petroleum / benzene), m. p. 138-140 °C; IR: 3356, 3174 (NH), 3025 (aryl-H), 2986, 2814 (alkyl-H), 1726, 1637 (C=O), 744, 700 Cm^{-1}. MS m/z (%): 295 (M^+, 0.1), 204 (M^+ -$PhCH_2$, 0.3), 176 (M^+-$COCH_2Ph$, 0.5), 136 (16), 92 (30), 91 ($PhCH_2$, 100), 65 (20). Anal. Calcd for $C_{18}H_{17}NO_3$: C, 73.20, H, 5.80; N, 4.74 %. Found; C, 73.32; H, 5.69; N, 4.82 %.

2-Phenylacetamide (8), (12-17 %), white crystals (benzene), m. p. 147-149 °C (lit.[18] m. p. 149-151 °C); IR: 3371, 3172 (NH), 3028 (aryl-H), 2943, 2814, 2728 (alkyl-H), 1639 (C=O), 742, 696 Cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.81 (br.s, 1, OH exchangeable), 3.59 (s, 2, CH_2), 5.44 (br.s, 2, NH_2 exchangeable), 5.77 (br.s, 1, NH exchangeable), 7.25-7.38 (m, 5, ArH). MS m/z (%): 135 (M^+, 17), 92 (83), 91 ($PhCH_2$, 100), 65 (28), 63 (11), 51 (11). Anal. Calcd for C_8H_9NO: C, 71.09; H, 6.71; N; 10.36 %. Found; C, 71.18; H, 6.61; N, 10.54 %.

Ethyl 1-(4-methoxybenzoyl)-6-oxo-2-thioxo-1,2,3,6-tetrahydropyrimidine-4-carboxylate (9), (69 %), yellow crystals (dioxane), m.p.226-228 °C; IR: 3444, 3145 (NH), 3064 (aryl-H), 2981, 2829, (alkyl-H),1743, 1695 (C=O), 1644, 1593, 1550 (C=N and / or C=C), 1157 (C=S), 805

Cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.28 (t, 3, $CH_2\underline{CH_3}$, *J*= 6.8, 7.2 Hz), 3.34 (br.s, 1, SH exchangeable),3.86 (s, 3, OCH_3), 4.27 (q, 2, $\underline{CH_2}CH_3$, *J*= 6.8 Hz), 6.75 (s, 1, CH=), 7.09 (d, 2, ArH, J_o= 9 Hz), 8.14 (d, 2, ArH, J_o= 9 Hz), 13.17 (br.s, 1, NH exchangeable). MS m/z (%): 334 (M^+, 3), 135 (COC_6H_4OMe-p, 59), 92 (30), 85 (100), 77 (34), 69 (17), 64 (36), 63 (24), 62 (14), 58 (20), 57 (45), 53 (34), 50 (17). Anal. Calcd for $C_{15}H_{14}N_2O_5S$: C, 53.89; H, 4.22; N, 8.38 %. Found: C**,** 53.77; H, 4.31; N, 8.24 %.

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