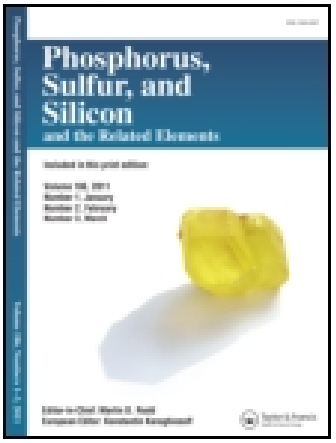

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Reaction of (E)-3-(Benzo[d][1,3]dioxol-5-yl)-2- Cyanoacryloyl Chloride with Nucleophilic Reagents Containing Nitrogen and Sulfur

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REACTION OF *(E)*-3-(BENZO[d][1,3]DIOXOL-5-YL)-2-CYANOACRYLOYL CHLORIDE WITH NUCLEOPHILIC REAGENTS CONTAINING NITROGEN AND SULFUR

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(E)-3-(Benzo[d][1,3]dioxol-5-yl)-2-cyanoacryloyl chloride was reacted with nucleophilic reagents containing nitrogen and sulfur to give new acryloyl amides, imides, thioesters, and heterocyclic systems. Some of these products showed moderate activities against antibacterial and antifungal agents.

Supplemental materials are available for this article. Go to the publisher's online edition of* Phosphorus, Sulfur, and Silicon and the Related Elements *to view the free supplemental file.

Keywords Benzimidazoles; benzothiazipines; 2-cyanoacryloyl chloride; pyrimidinethiones

INTRODUCTION

The recent widespread uses of 2-acryloyl chloride derivatives in the synthesis of highly important products, such as precursors of herbicides,[1,2] antifungal,[3] and pharmaceutical intermediates[4] make them worthy to be studied and encouraged us to use new derivatives of these categories in the synthesis of new analogous of 2-acryloyl amides[5] and esters,[6–9] besides many interesting biologically and pharmacologically active heterocyclic systems, such as benzimidazoles,[10,11] benzthiazoles,[12] benzothiazepines,[13,14] and pyrimidinethiones.[15]

RESULTS AND DISCUSSION

In continuation of our previous studies,[16–20] we report in this article the reactions of (*E*)-3-(benzo[d][1,3]dioxol-5-yl)-2-cyanoacryloyl chloride[16] (**3**; prepared as mentioned in Scheme 1) with some nucleophilic reagents containing sulfur and nitrogen. The present investigation was planned to study the effect of the 2-cyano group on the reactivity and stability of C_2—C_3 double bond towards different strong to weak nucleophiles, besides

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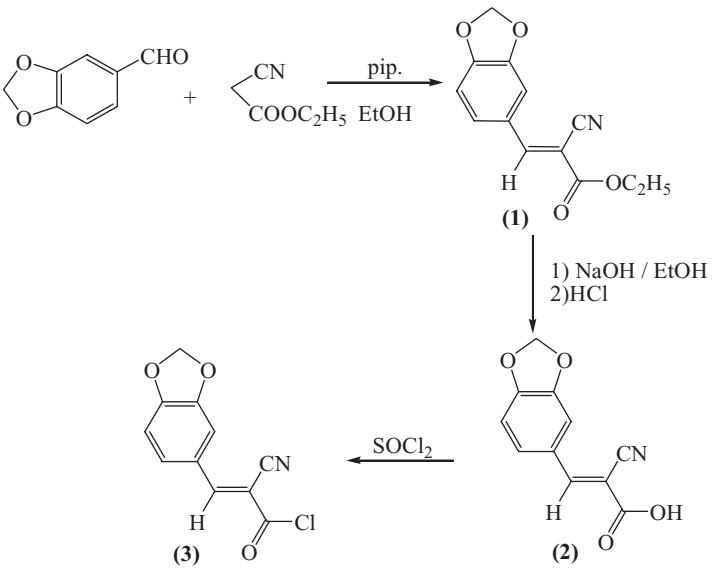
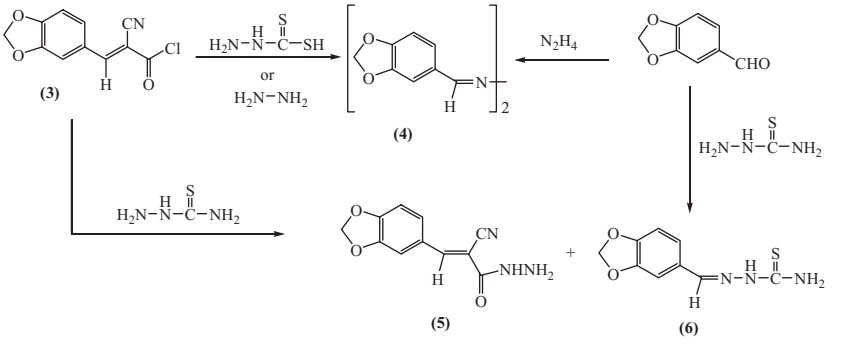


Scheme 1

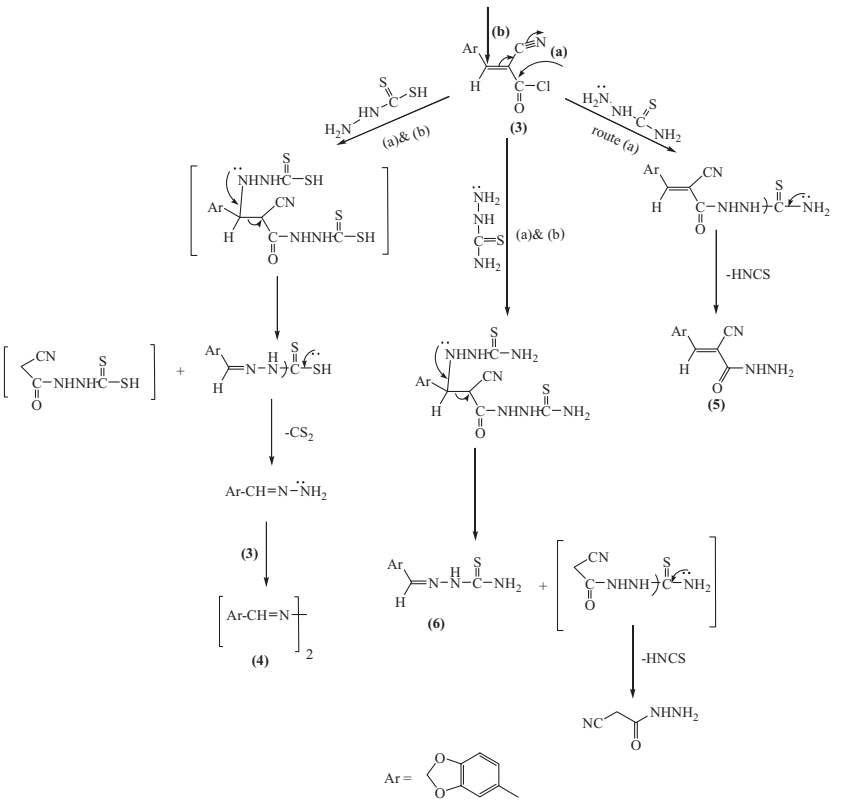
its enhancement of nucleophilic addition at C_2-C_3 double bond to give new heterocyclic derivatives.

Treatment of **3** with hydrazine hydrate[16] and/or hydrazinecarbodithioc acid yielded the aldazine[21] (**4**) as sole product, while with thiosemicarbazide (**3**) gave a mixture of 2-propenoyl hydrazide derivative (**5**) and piperonal thiosemicarbazone[22,23] (**6**) (Scheme 2).



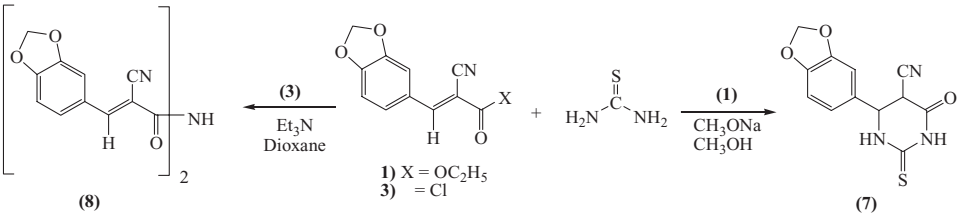
Scheme 2

Formation of these products can be explained according to the following pathway:



The structures of aldazine[21] (**4**) and carbazone[22,23] (**6**) were established by comparison with authentic samples prepared by condensation of piperonal with hydrazine hydrate and/or thiosemicarbazide, in addition to spectral data.

Li et al.[24,25] condensed the ester[16] (**1**) with thiourea in the presence of sodium methoxide or K_2CO_3 to give 4-oxo-2-thioxohexahydropyrimidine derivative (**7**) (in cis/trans forms) in excellent yield (Scheme 3). In condensation of the acid chloride (**3**) with thiourea in the presence of Et_3N as a base, only the imide (**8**) was isolated in pure form (Scheme 3).



Scheme 3

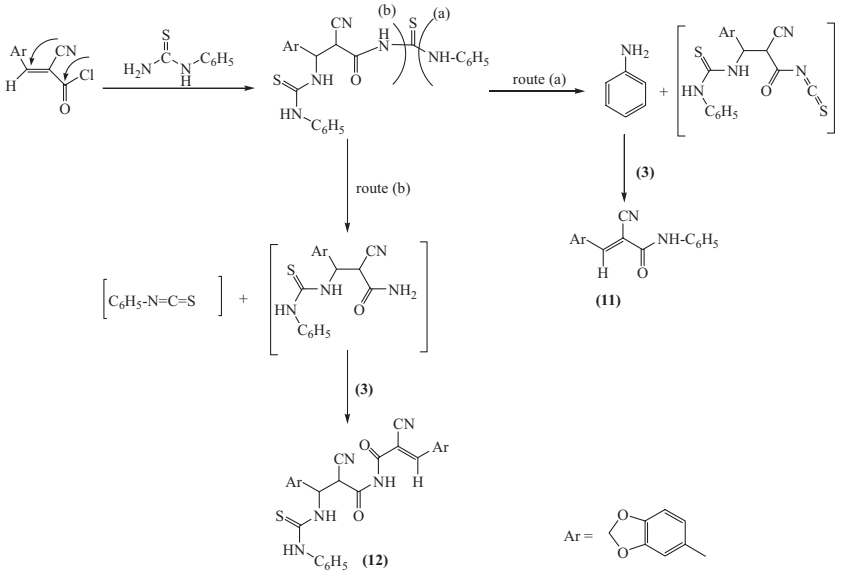
Condensation of ester (**1**) with N-methyl thiourea in sodium methoxide afforded a mixture of 4-oxo-2-thioxopyrimidine derivative[25] (**9**) (cis/trans form 50:50) and the transesterification[26] product (*E*)-methyl 3-(benzo[d][1,3]dioxol-5-yl)-2-cyanoacrylate (**10**)

(Scheme 4). On the other hand, treatment of acid chloride (**3**) with N-methyl thiourea gave only the pyrimidinthione (**9**) (Scheme 4).

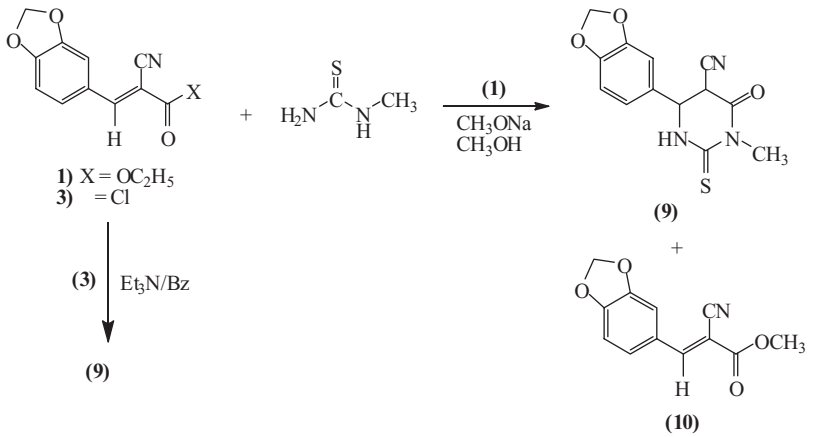
Condensation of (**3**) with phenyl thiourea in the presence of Et_3N yielded a mixture of amide (**11**) and imide (**12**) (Scheme 5).

The structure of amide (**11**) was established chemically by condensation of (**3**) with aniline under the same condition (Scheme 5). Also, this compound was prepared by condensation of piperonal with N-phenyl cyanoacetamide in the presence of a base[27] (Scheme 5).

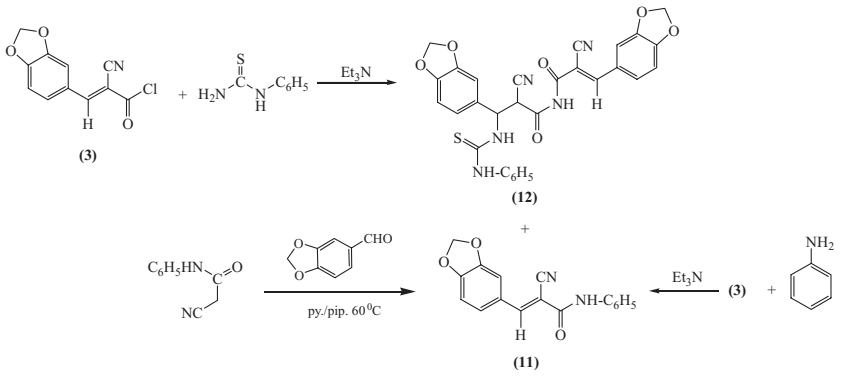
Formation of **11** and **12** can be explained according to the following pathway:



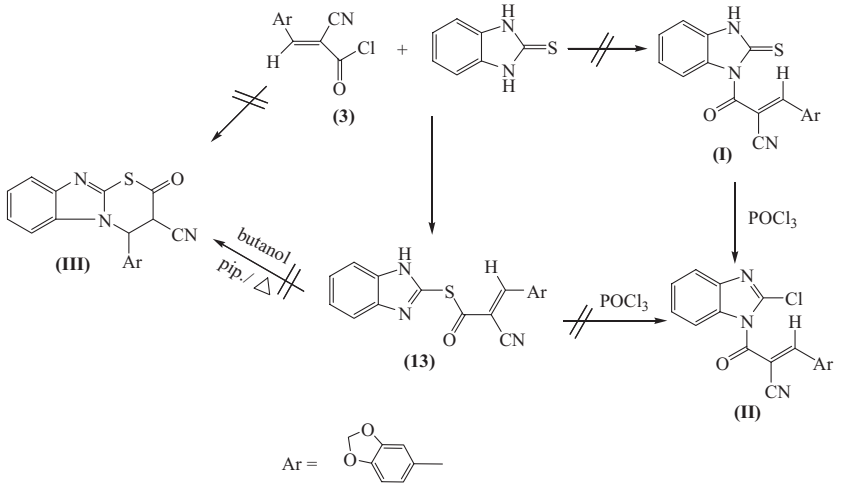
Condensation of **3** with benzimidazolethione in boiling dioxane and/or heating without solvent at 140°C afforded the thioester (**13**) (Scheme 6). Formation of S-acyl (**13**) rather than N-acyl derivative (**I**) was established chemically by heating of **13** with $POCl_3$ to give



Scheme 4



Scheme 5

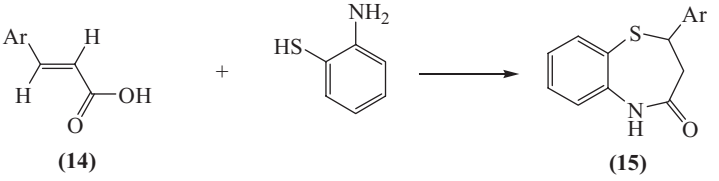


Scheme 6

unchanged product instead of the expected 2-chloro-benzimidazole derivative (**II**) (Scheme 6). Also, in contrast to Britsun et al.,[28–30] this reaction gave only the open product **13** rather than the cyclic product (**III**). Refluxing of **13** in butanol in the presence of piperidine and/or pyridine failed to give the cyclic system (**III**) (Scheme 6).

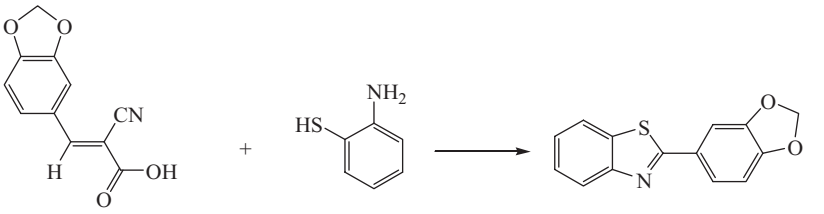
This supports our previous studies[17] about the highest reactivity of S versus N.

Reaction of cinnamic acid derivatives (**14**) with 2-amino thiophenol in the presence of a base[31–37] afforded the 1,5-benzothiazepine-4-ones (**15**) (Scheme 7).



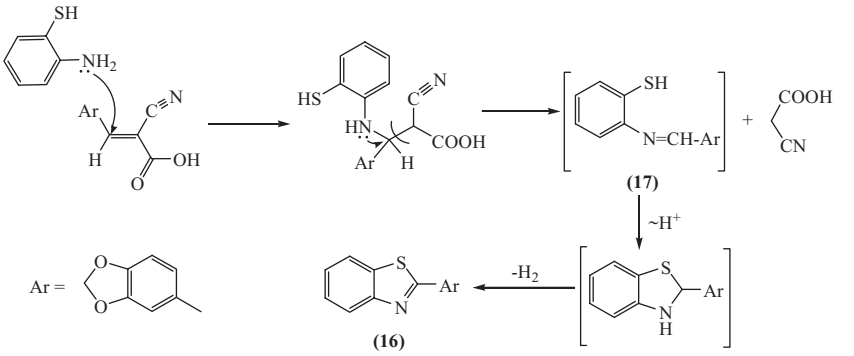
Scheme 7

When we repeat this reaction with our starting material 2-cyanopropenoic acid derivative (**2**) in different conditions, we get 2-(benzo[d][1,3]dioxol-5-yl)benzo[d]thiazole[12] (**16**) as the sole product (Scheme 8).



Scheme 8

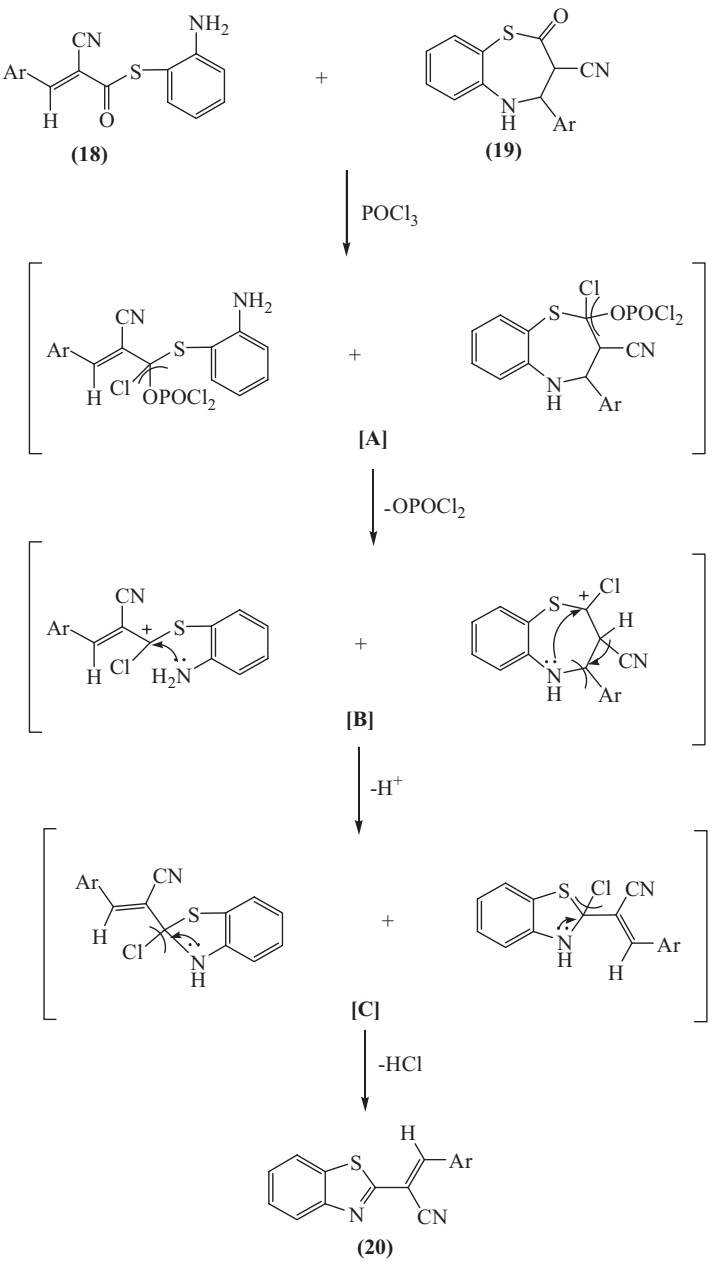
Formation of (**16**) established the idea about the effect of a cyano group on the reactivity of α,β-unsaturated double bond towards nucleophilic reagents, which facilitates the C—C bond cleavage with formation of the imine (**17**), which then undergoes ring closure with subsequent oxidation under reaction conditions to give **16** as shown on the following pathway:



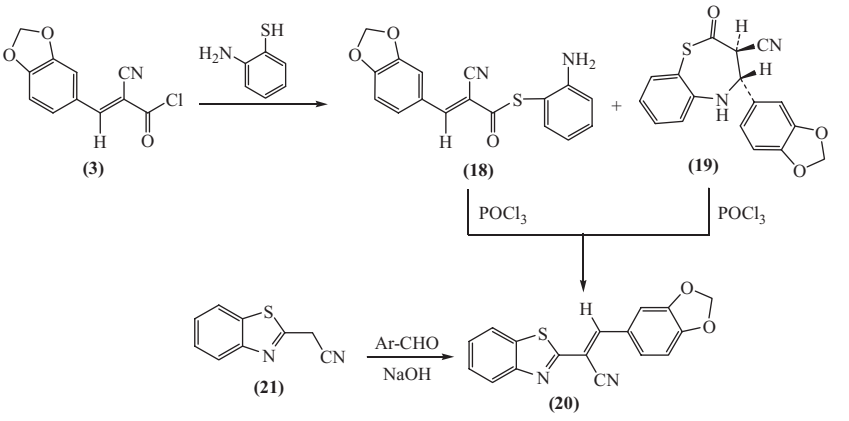
When we carried the condensation reaction of 2-propenoyl chloride (**3**) with 2-amino thiophenol in the presence of Et_3N at room temperature, a mixture of thiopropenoate derivative (**18**) and 1,5-benzothiazepin derivative (**19**) was obtained (Scheme 9). Compound **19** was identified in a mixture of **18** and **19** by ^{1}H NMR. Treatment of both pure **18** and **18** + **19** mixture with $POCl_3$ afforded the same benzothiazole derivative (**20**) as a sole product (Scheme 9).

The structure of benzothiazole (**20**) was established chemically by condensation of 2-cyanomethylbenzthiazole (**21**) with piperonal in the presence of NaOH as a base.[38]

Formation of benzthiazole (**20**) can be achieved according to the following pathway:



The $POCl_3$ attacks the carbonyl carbon atom to give the intermediate[39] [A], which lost $OPOCl_2$ to give the carbocation [B]. [Conformational analysis[40] for the most stable conformer [B], (Figure S1, Supplemental Materials, available online) shows that the nitrogen atom at position 5- is very near to the carbon 2- (3.22 A°)]. Nucleophilic attack of the N atom into the carbocation with ring contraction gave the intermediate [C], which lost HCl to give benzthiazole (**20**).



Scheme 9

Measurement of Antimicrobial and Antifungal Activities Using Diffusion Disc Method

Antimicrobial activity was measured in the Microanalytical Center, Cairo University, Giza, Egypt.

Method

A filter paper sterilized disc saturated with measured quantity of the sample with concentration of 20 mg/mL was placed on a plate containing solid bacterial medium (nutrient agar broth) or fungal medium (Dox's medium), which was heavily seeded with the spore suspension of the tested organism. After inoculation, the diameter of the clear zone of inhibition surrounding the sample was taken as a measure of the inhibitory power of the sample against the particular test organism.[41–44] The experimental details and results are summarized in the Supplemental Materials (Table S1).

EXPERIMENTAL

Melting points reported are uncorrected. IR spectra were recorded on Pye Unicam SP 1200 spectrophotometer using the KBr wafer technique. ^{1}H NMR spectra were determined on a Varian FT-200 and a Bruker AC-300 MHz using TMS as internal standard. All chemical shifts (δ) are expressed in ppm. All the NH or OH protons disappeared upon addition of D_2O. The mass spectra were determined using an MP model MS-5988 and a Shimadzu single focusing mass spectrophotometer (70 eV). Elemental analyses were investigated by an Elementar analyzer Vario EL III.

(E)-3-(Benzo[d][1,3]dioxol-5-yl)-2-cyanoacryloyl chloride (3)

A mixture of (*E*)-3-(benzo[d][1,3]dioxol-5-yl)-2-cyanoacrylic acid (10 g) and thionyl chloride (15 mL) was heated on a water bath for 3 h. The excess $SOCl_2$ was distilled under reduced pressure, and the solid separated was collected, triturated with petroleum ether 40–60°C, dried, and crystallized to give **3**.

(2E,N'E)-3-(Benzo[d][1,3]dioxol-5-yl)-N'-(benzo[d][1,3]dioxol-5-ylmethylene)-2-cyanoacrylohydrazide (4)

To a solution of **3** (1.18 g, 0.005 mol) in dioxane (20 mL) in the presence of triethylamine (0.505 g, 0.005 mol), hydrazinecarbodithioc acid (0.45 g, 0.005 mol) was added. The reaction mixture was refluxed for 1 h. The solid formed (Et_3NHCl) was filtered, and the filtrate was concentrated. The remaining semisolid was crystallized from petroleum-ether (80–100°C) to give **4** as yellow crystals; mp: 179–180°C, yield 79%. IR (ν): absence of NH, CN, CO. ^{1}H NMR(DMSO-d_6) δ 6.09 (s, 4H, 2 × O—CH_2—O), 7.38 (s, 2H), 7.00 (d, J = 7.8, 2H), 7.33 (d, J = 8.1, 2H), 8.56 (s, 2H, 2 × = CH). MS: 296 ([M]$^{+\cdot}$, 100), 269 (78), 175 (53), 174 (10), 152 (25), 148 (33). Anal. Calcd. for $C_{16}H_{12}N_2O_4$ (296.28): C, 64.86; H, 4.08; N, 9.45. Found: C, 65.01; H, 4.23; N, 9.67.

(E)-3-(Benzo[d][1,3]dioxol-5-yl)-2-cyanoacrylohydrazide (5) and 1-(Benzo[d][1,3] dioxol-5-ylmethylene)thiosemicarbazide (6)

To a solution of **3** (1.18 g, 0.005 mol) in dioxane (20 mL) in the presence of triethylamine (0.505 g, 0.005 mol), thiosemicarbazide (0.45 g, 0.005 mol) was added. The reaction mixture was refluxed for 1 h. The solid formed was filtered, and the filtrate was concentrated. The remaining semisolid was triturated with boiling petroleum-ether (60–80°C) to give **6** as yellow crystals, and the insoluble solid was crystallized from toluene to give **5** as yellow crystals.

5: Mp: 181–182°C, yield 56%. IR (ν): 3420 (NH, NH_2), 2212 (CN), 1623 (C=O) cm^{-1}. ^{1}H NMR(DMSO-d_6) δ 6.05 (s, 2H, O—CH_2—O), 6.89 (d, CH J = 6.9, 1H), 6.92 (d, CH J = 8.9, 1H), 7.62 (s, 1H, CH), 7.95 (s, 1H, CH), 7.99 (s, 1H, NH), 8.07 (s, 1H, NH), 11.28 (s, 1H, NH). MS: 231 ([M]$^{+\cdot}$, 72), 230 (34), 219 (14), 190 (19), 175 (21), 174 (49), 165 (20), 164 (17), 147 (30), 86 (100). Anal. Calcd. for $C_{11}H_9N_3O_3$ (231.202): C, 57.14; H, 3.92; N, 18.17. Found: C, 57.34; H, 3.72; N, 18.26.

Compound **6** was established by authentic sample[22,23] prepared by condensation of piperonal with thiosemicarbazide.

(2*E*)-3-(1,3-Benzodioxol-5-yl)-N-[(2*E*)-3-(1,3-benzodioxol-5-yl)-2-cyanoprop-2-eno-yl]-2-cyanoacrylamide (8)

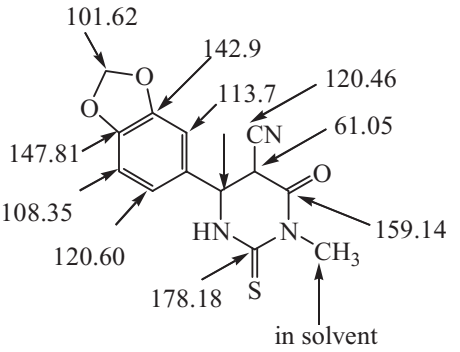
To a solution of **3** (1.18 g, 0.005 mol) in dioxane (20 mL) in the presence of triethylamine (0.505 g, 0.005 mol), thiourea (0.38 g, 0.005 mol) was added. The reaction mixture was refluxed for 3 h. The solid formed was filtered, and the filtrate was concentrated. The remaining semisolid was crystallized from petroleum-ether (80–100°C) to give **8** as yellow crystals; mp: 159–160°C, yield 45%. IR (ν): br. 3425 (NH), 2213 (CN), 1736 (C=O) cm^{-1}. ^{1}H NMR(DMSO-d_6) δ 6.13 (s, 4H, 2 × O—CH_2—O), 7.08 (d, J = 7.8, 2H), 7.53 (d, J = 6.9, 2H), 7.62 (s, 2H), 8.14 (s, 2H, = CH), 8.53 (br.s, 1H, NH). MS: 415 [M$^{+\cdot}$], 217 (100), 172 (32), 142 (10), 114 (27). Anal. Calcd. for $C_{22}H_{13}N_3O_6$ (415.34): C, 63.62; H, 3.15; N, 10.12. Found: C, 63.42; H, 3.24; N, 10.03.

6-(Benzo[d][1,3]dioxol-5-yl)-1-methyl-4-oxo-2-thioxo-hexahydropyrimidine-5-carbonitrile (9)

To a solution of **3** (1.18 g, 0.005 mol) in dry benzene (50 mL) in the presence of triethylamine (0.505 g, 0.005 mol), N-methyl thiourea (0.45 g, 0.005 mol) was added, and the reaction mixture was refluxed for 40 min. The solid formed was collected, washed with water

(80 mL), dried, and crystallized from toluene to give **9** as yellow crystals; mp: 239–240°C, yield 74%. IR (ν): 3384 (NH), 2208 (CN), 1682 (C=O) cm^{-1}. ^1H NMR(DMSO-d_6) δ cis/trans 3.47 (s, 3H, N−CH_3), 3.56 (s, 3H, N−CH_3), 5.07–5.13 (d,d, 2H), 6.07 & 6.16 (s, 2H), 7.24 & 7.22 (s, 1H), 6.89–7.13 (m, 2H), 10.35 (s, 1H, NH). MS: 289 ($M^{+\cdot}$, 67), 288 ([M-1]$^{+\cdot}$, 100), 287 ([M-2]$^{+\cdot}$, 5), 260 (10), 232 (4), 215 (12), 200 (47), 174 (4), 145 (5). Anal. Calcd. for $C_{13}H_{11}N_3O_3S$ (289.306): C, 53.47; H, 3.83; N, 14.52. Found: C, 53.57; H, 3.73; N, 14.61.

^{13}C NMR (DMSO-d_6):



(E)-Methyl 3-(benzo[d][1,3]dioxol-5-yl)-2-cyanoacrylate (10)

To a solution of (E)-3-(benzo[d][1,3]dioxol-5-yl)-2-cyanoacrylate (**1**) (1.22 g, 0.005 mol) in methanol (20 mL) and sodium methoxide in methanol (0.54 mL, 0.01 mol), N-methyl thiourea (0.45 g, 0.005 mol) was added. The mixture was stirred at room temperature for 1 h. The solid formed was filtered, and the filtrate was acidified by 5% acetic acid. Then the solid formed was collected, washed with water (50 mL), dried, and crystallized from toluene to give **9** as yellow crystals, and then from ethanol to give **10** as yellow crystals; mp: 119–120°C. IR (ν): 2218 (CN), 1726 (C=O) cm^{-1}. ^1H NMR(DMSO-d_6) δ 3.84 (s, 3H, OCH_3), 6.18 (s, 2H, O−CH_2−O), 7.68 (s, 1H, Ar-H), 7.15 (d, 1H, J = 6.3, Ar-H), 7.64 (d, 1H, J = 4.8, Ar-H), 8.28 (s, 1H, =CH). MS: 232 ([M+2]$^{+\cdot}$, 14), 231 ([M]$^{+\cdot}$, 100), 230 (([M-1]$^{+\cdot}$, 42), 200 (27), 199 (12), 171 (247), 170 (62), 142 (27), 114 (60).

(E)-3-(Benzo[d][1,3]dioxol-5-yl)-2-cyano-N-phenylacrylamide (11) and *(E)*-1-(1-(Benzo[d][1,3]dioxol-5-yl)-3-(3-(benzo[d][1,3]dioxol-5-yl)-2-cyanoacrylamido)-2-cyano-3-oxopropyl)-3-phenylthiourea (12)

To a solution of **3** (1.18 g, 0.005 mol) in dioxane (30 mL) in the presence of triethyl amine (0.505 g, 0.005 mol), phenyl thiourea (0.76 g, 0.005 mol) was added, and the reaction mixture was refluxed for 1h. The solid formed was filtered, and the filtrate was concentrated. The remaining semisolid was crystallized from petroleum-ether 80–100°C to give **11** as yellow crystals and then from toluene to give **12** as yellow crystals.

11: Mp: 88–90°C, yield 70%. IR (ν): 3341 (NH), 2212 (CN), 1678 (C=O) cm^{-1}. MS: 292 ($M^{+\cdot}$, 13), 291 ([M-1]$^{+\cdot}$, 33), 290 (M-2]$^{+\cdot}$, 8), 215 (1), 200 (100), 170 (95), 142 (42). Anal. Calcd. for $C_{17}H_{12}N_2O_3$ (292.29): C, 69.85; H, 4.14; N, 9.59. Found: C, 69.87; H, 4.24; N, 9.49.

12: Mp: 118–120 °C, yield 30%. IR (ν): 3328, 3320, 3238 (NH), 2217 (CN), 1709, 1674 (C=O) cm^{-1}. MS: 551 ($[M\text{-}OH]^{+\cdot}$, 0.2), 550 (4), 521 (1), 491 (0.3), 445 (0.5), 429 (0.3), 328 (0.3), 226 (6), 225 (24), 200 (1), 172 (3), 144 (2), 136 (16), 135 (100), 192 (0.8). Anal. Calcd. for $C_{29}H_{12}N_5O_6S$ (567.566): C, 61.36; H, 3.73; N, 12.34. Found: C, 61.46; H, 3.63; N, 12.44.

Reaction of (3) with Aniline, Formation of 11

To a solution of **3** (1.18 g, 0.005 mol) in dry benzene (50 mL) in the presence of triethyl amine (0.505 g, 0.005 mol), aniline (0.46 gm, 0.005 mol) was added, and the reaction mixture was refluxed for 1 h. The solid separated was filtered, washed with water (80 mL), dried, and crystallized from petroleum-ether 80–100°C to give **11**.

(E)-S-1H-Benzo[d]imidazol-2-yl 3-(Benzo[d][1,3]dioxol-5-yl)-2-cyanoprop-2-enethi-oate (13)

A mixture of **3** (1.18 g, 0.005 mol) and benzimidazolethione (0.75 g, 0.005 mol) was heated without solvent at 140–150°C for 30 min. The solid was triturated with ethanol, collected, and crystallized from toluene to give **13** as orange crystals; mp: 211–212°C, yield 82%. IR (ν): 3155 (NH), 2218 (CN), 1688 (C=O) cm^{-1}. ^{1}H NMR(DMSO-d_6) δ 6.18 (s, 2H, O—CH_2—O), 7.12 (m, 4H, Ar-H), 7.48–7.70 (m, 3H, Ar-H), 8.21 (s, 1H, = CH), 9.27 (s, 1H, NH). MS: 348 ($[M\text{-}1]^{+\cdot}$, 25), 347 ($[M\text{-}2]^{+\cdot}$, 94), 346 $(M\text{-}3]^{+\cdot}$, 100), 260 (18), 188 (8), 173 (40), 172 (34). Anal. Calcd. for $C_{18}H_{11}N_3O_3S$ (349.298): C, 61.89; H, 3.17; N, 12.03. Found: C, 61.78; H, 3.27; N, 11.93.

2-(Benzo[d][1,3]dioxol-5-yl)benzo[d]thiazole (16)

A mixture of (E)-3-(benzo[d][1,3]dioxol-5-yl)-2-cyanoacrylic acid **2** (1.18 g, 0.005 mol) and 2-amino thiophenol (0.5 mL, 0.001 mol) was heated without solvent at 160–180°C for 2 h. The solid was triturated with diethyl ether, collected, and crystallized from petroleum ether 80–100°C to give **16** as yellow crystals; mp: 181–182°C, yield 78%. IR (ν): absence of NH, CN, CO. ^{1}H NMR(DMSO-d_6) δ 6.14 (s, 2H, O—CH_2—O), 7.07 (d, 1H, J = 2.1), 7.59–8.08 (m, 4H, Ar-H), 7.6 (d, 1H, J = 1.5), 7.59 (d, 1H, J = 1.2). Anal. Calcd. for $C_{14}H_9NO_2S$ (255.286): C, 65.86; H, 3.55; N, 5.49. Found: C, 65.66; H, 3.75; N, 5.35.

(E)-S-2-aminophenyl 3-(Benzo[d][1,3]dioxol-5-yl)-2-cyanoprop-2-enethioate (18) and (3R,4R)-4-(Benzo[d][1,3]dioxol-5-yl)-2-oxo-2,3,4,5-tetrahydrobenzo[b][1,4]thiazep-ine-3-carbonitrile (19)

To a solution of **3** (2.36 g, 0.01 mol) in dry benzene (50 mL) in the presence of triethylamine (1.39 g, 0.01 mol), 2-amino thiophenol (1 mL, 0.01 mol) was added, and the reaction mixture was stirred for 1 h. The solid separated was filtered, washed with water (80 mL), dried, and crystallized from petroleum-ether 60–80°C to give **18** as yellow crystals, then the insoluble solid was crystallized from toluene to give **19** as yellow crystals.

18: Mp: 159–160°C, yield 30%. IR (ν): 3330 (NH), 2200 (CN), 1686 (C=O) cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 6.2 (s, 2H, O—CH_2—O), 7.13 (d, J = 8.1, $1H_{pip.}$), 7.25–7.38 (m, 4H, Ar-H), 7.56 (d, J = 8.4, 1H), 7.63 (s, $1H_{pip.}$), 8.20 (s, 1H), 10.02 (s, 2H, NH_2). MS:

323 ([M-1]$^{+\cdot}$, 15), 322 ([M-2]$^{+\cdot}$, 44). Anal. Calcd. for $C_{17}H_{12}N_2O_3S$ (324.356): C, 62.95; H, 3.73; N, 8.64. Found: C, 62.85; H, 3.83; N, 8.45.

18 + 19: ^{1}H NMR (DMSO-d_6) δ 4.57 (d, CH J = 12.3, 1H), 5.12 (d, CH J = 12.3, 1H), 5.85 (s, 2H, O—CH_2—O), 6.87 (s, 1H, $CH_{pip.}$), 7.23 (d, $CH_{pip.}$ J = 8.7, 1H), 7.15–7.65 (m, 4H, Ar-H), 10.49 (s, 1H, NH). MS: 324 ([M]$^{+\cdot}$, 10), 323 ([M—1]$^{+\cdot}$, 7). Anal. Calcd. for $C_{17}H_{12}N_2O_3S$ (324.356): C, 62.95; H, 3.73; N, 8.64. Found: C, 63.05; H, 3.64; N, 8.73.

(E)-3-(Benzo[d][1,3]dioxol-5-yl)-2-(benzo[d]thiazol-2-yl) acrylonitrile (20)

A mixture of **18** and/or a mixture of **18 + 19** (2 g) with $POCl_3$ (10 mL) was heated on a water bath for 6 h. After cooling, the reaction mixture was poured onto crushed ice (50 g). The solid separated was filtered, washed with water (50 mL), dried, and crystallized from toluene to give **20** as yellow crystals; mp: 219–220°C, yield 70–90%. IR (ν): 2211 (CN) cm^{-1}. ^{1}H NMR(DMSO-d_6) δ 6.19 (s, 2H, OCH_2O), 7.15 (d, $1H_{pip.}$, J = 8.4), 7.49 (t, $1H_{arm.}$, J = 6.6, 7.5), 7.57 (t, $1H_{arm.}$, J = 6.9, 7.8), 7.66 (d, $1H_{pip.}$, J = 8.4), 7.72 (s, $1H_{pip.}$), 8.04 (t, $1H_{arm.}$, J = 8.1), 8.14 (s, $1H_{arm.}$, J = 8.1), 8.29 (s, 1H, = CH). Anal. Calcd. for $C_{17}H_{10}N_2O_2S$ (306.336): C, 66.56; H, 3.29; N, 8.64. Found: C, 66.74; H, 3.69; N, 8.73.

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