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Synthesis and Reactions of 2-[(methylsulfanyl) (phenylamino) and 2-[(methylsulfanyl)(N-methylphenylamino) methylidene]-1,3-diphenyl- propane-1,3-dione

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A B S T R A C T

The objective of this research is to investigate the potential applications of 1,3-diphenylpropane-1,3-dione (**1**) in the synthesis of novel heterocyclic compounds. This can be achieved by combining 1,3-diphenylpropane-1,3-dione (**1**) with phenyl isothiocyanate in dimethylformamide while potassium hydroxide is present. An equimolar quantity of methyl iodide is subsequently incorporated, yielding 2-[(methylsulfanyl) (phenylamino) methylidene]-1, 3-diphenylpropane-1,3-dione (**3**). Contrarily, the addition of two equimolar amounts of methyl iodide resulted in the formation of 2-[(methylsulfanyl) (*N*-methylphenylamino) methylidene]-1,3-diphenylpropane-1,3-dione (**4**), which used as starting materials. When chemical compound **3** was combined with hydrazine and phenylhydrazine in refluxing ethanol, it resulted in (phenylamino)-1*H*-pyrazole derivatives **27a,b**. Chemical **3** combines with 3-phenyl-5-amino-(1*H*)-pyrazole (**6**) and 2-aminobenzimidazole (**7**), aminopyrazole derivatives **10a-c**, to form, pyrazolo[1,5-*a*]pyrimidine derivative **8** and pyrimido [1,2-a]benzimidazole derivative **9**, compounds **12a-c**, respectively. Moreover, component **4** can be treated with urea, thiourea, 2-aminopyridine (**15**) and 2-aminobenzothiazole (**16**) resulting in the corresponding 2-hydroxy-6-phenylpyrimidine derivative **13**, and 4-phenyl-2-thioxopyrimidine derivative **14**, compounds **17** and **18**. Additionally, ingredient **1** produces pyridine-3-carbonitrile equivalents **22a-c** through its interaction with arylidenemalononitriles **19a-c**.

1. Introduction

The biological functions and pharmacological efficacy of heterocyclic chemicals have drawn attention to them. Therefore, the goal of this current endeavor is to produce several novel heterocyclic compounds with anticipated biological activity. Additionally, the intriguing pharmaceutical compound 1,3-diphenylpropane-1,3-dione (1) will be discussed. It has been found to be a highly potent anti-mutagenic agent [1]. Has shown potential as a chemo-preventive agent for breast cancer [2] and has also been found to disrupt the cell cycle in human prostate cancer cells [3]. Recent research has also revealed

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that derivatives of 1,3,4-thiadiazole possess strong anti-inflammatory properties [4-6], as well as potential as antispasmodic [6-8] and antimicrobial medications [9]. Furthermore, studies have shown that thiophene compounds possess anti-amoebic properties [10], molluscicidal effects [11], and anti-inflammatory effects [12]. In line with our laboratory's ongoing research strategy to synthesize a range of heterocyclic ring systems for biological screening [13-17], we have undertaken an investigation into the potential of 1,3-diphenyl propane-1,3-dione (1) as a reactive synthon for the desired compounds.

2. Experimental

2.1. Instruments

The melting points of each substance were measured using a Gallenkamp melting point instrument. The infrared spectra of potassium bromide discs were acquired using a Shimadzu FT IR 8101 PC spectrophotometer and a Pye Unicam SP 3300. The NMR spectra in dimethyl sulphoxide (DMSO-d_6) or deuterated chloroform ($CDCl_3$) were captured using a Varian Mercury VXR-300 spectrometer. ^{1}H spectra were recorded at 300 MHz, and the chemical shifts were assigned accordingly. To obtain the mass spectra for this study at 70 eV, we utilized the Shimadzu GCMS-QP 5000 EI and Shimadzu GCMS-QP 1000 EX mass spec-trometers. The elemental analyses, as well as the previously described ones, were conducted by the Cairo University Micro-analytical Centre in Giza, Egypt, and the Al-Azhar University Regional Centre for Mycology and Biotechnology in Cairo, Egypt.

2.2. Organic Preparation

1,3-Diphenylpropane-1,3-dione (**1**), m.p. 77-78ºC [18], 3-Phenyl-5-amino-(1*H*)-pyrazole (**6**), m.p. 124ºC [19], 3-Amino-4-arylhydrazono-5-imino-2-pyrazolines **10a-c** [20] and Cinnamonitriles **19a-c** [21] were created using strategies described in the scientific literature.

2.3. Organic Synthesis and Reactions

2.3.1. Reaction of 1,3-diphenylpropane-1,3-dione (1) with phenyl isothiocyanate and methyl iodide

The typical process involved adding 2.24 g (10 mmol) of 1,3-diphenylpropane-1,3-dione (**1**) to a stirred solution of potassium hydroxide (0.56 g, 10 mmol) in 30 ml of dimethyl formamide. The mixture was stirred for 30 minutes at ambient level before adding 1.35 g of phenyl isothiocyanate (10 mmol). After this, the mixture was blended for an additional 6 hours, during which either 1.41 g (10 mmol) or 2.82 g (20 mmol) of methyl iodide was incorporated until all starting materials were used up. To obtain the corresponding ingredients **3** and **4**, the precipitated material was filtered, rinsed using water, dried, and recrystallized from ethanol. Below is a list of 3 and 4's physical and spectral characteristics:

2-[(Methylsulfanyl)(phenylamino)methylidene]-1,3-diphenylpropane-1,3-dione (**3**): Yield 88%; m.p.98ºC (EtOH/H_2O) [lit.22 m.p.97^{0}C]; IR (KBr) νmax/cm^{-1}: 3150 (NH), 1670, 1650 (2C=O); ^{1}H NMR (DMSO-d_6):δ 2.03 (s, 3H, CH_3), 7.01-8.19 (m, 15H, Ar-H), 10.79 (s, 1H, NH); MS m/z (%): 373 (M^+, 6.1), 326 (6.1), 105 (62.2), 77 (100); Analysis for $C_{23}H_{19}NSO_2$ (373.47): Calcd.: C, 73.97; H, 5.13; N, 3.75; S, 8.59%; Found: C, 73.98; H, 5.12; N, 3.77; S, 8.57%.

2-[(Methylsulfanyl)(*N*-methylphenylamino)methylidene]-1,3-diphenylpropane-1,3-dione (**4**): Yield 89%; m.p.122^{0}C (EtOH/H_2O); IR (KBr) νmax/cm^{-1}: 1666, 1649 (2C=O); ^{1}H NMR (DMSO-d_6):δ 2.07 (s, 3H,

CH_3), 2.40 (s, 3H, CH_3), 7.03-8.19 (m, 15H, Ar-H); MS m/z (%): 387 (M^+, 1.9), 326 (9.8), 105 (33), 77 (100); Analysis for $C_{24}H_{21}NSO_2$ (387.50): Calcd.: C, 74.39; H, 5.46; N, 3.61; S, 8.28%; Found: C, 74.36; H, 5.49; N, 3.64; S, 8.30%.

Reaction of 2-[(methylsulfanyl)(phenylamino) methylidene]-1,3-diphenylpropane-1,3-dione (3) with hydrazine derivatives

Standard Operating Procedure: Either 2 mmol of hydrazine or 2 mmol of phenylhydrazine was added to a solution of **3** (0.746 g, 2 mmol) in 20 ml of ethanol. The outcome combination was refluxed for four hours and then allowed to cool to ambient temperature. The resulting solid material was filtered out, cleaned with ethanol, and dried. Re-crystallization using the appropriate solvent produced the corresponding analogues of phenylaminopyrazoles, **5a** and **5b**, respectively. The physical and spectral information for **5a** and **5b** are as follows:

4-Benzoyl-3-phenyl-5-(phenylamino)-1*H*-pyrazole (**5a**); Yield 91%; m.p.115^{o}C (EtOH/DMF); IR (KBr) νmax/cm^{-1}: 3331, 3169 (2NH), 1640 (C=O); ^{1}H NMR (DMSO-d_6):δ 6.90-7.86 (m, 15H, Ar-H), 9.06 (s, 1H, NH), 13.07 (s, 1H, NH); MS m/z (%): 339 (M^+, 39.3), 233 (3.7), 105 (6.1), 77 (100); Analysis for $C_{22}H_{17}N_3O$ (339.39): Calcd.: C, 77.86; H, 5.05; N, 12.38%; Found: C, 77.84; H, 5.07; N, 12.40%.

4-Benzoyl-1,3-diphenyl-5-(phenylamino)-1*H*-pyrazole (**5b**): Yield 90%; m.p.156^{o}C (EtOH/DMF); IR (KBr) νmax/cm^{-1}: 3316 (NH), 1644 (C=O); ^{1}H NMR (DMSO-d_6):δ 6.89-7.72 (m, 20H, Ar-H), 9.13 (s, 1H, NH); MS m/z (%): 415 (M^+, 100), 338 (8.88), 208 (10.6), 105 (24.44), 77 (72.21); Analysis for $C_{28}H_{21}N_3O$ (415.49): Calcd.: C, 80.94; H, 5.09; N, 10.11%; Found: C, 80.97; H, 5.07; N, 10.15%.

Reaction of 2-[(methylsulfanyl)(phenylamino)methyl- idene]-1,3-diphenylpropane-1,3-dione (3) with heterocyclic amines

Common working approach: After refluxing for seven hours in ethanol (15 ml) with a few drops of piperidine, an amalgam of **3** (0.746 g, 2 mmol) and the proper heterocyclic amine, 3-phenyl-5-amino-(1*H*)-pyrazole (**6**) (2 mmol) or 2-aminobenzimidazole (**7**) (2 mmol), was let cool to atmospheric temperature. After the precipitate had formed, the product was passed through a filter, purified via ethanol, and drained. Chemicals **8** and **9** were obtained, respectively, through recrystallization using a suitable solvent. The following is a list of the chemicals **8** and **9** physical as well as spectroscopic information.

2,7-Diphenyl-5-(phenylamino)-6-benzoylpyrazolo[1,5-*a*]pyrimidine (**8**): Yield 75%; m.p.275^{o}C (EtOH/DMF); IR (KBr) νmax/cm^{-1}: 3375, (NH), 1636 (C=O); ^{1}H NMR (DMSO-d_6):δ 6.87 (s, 1H, CH), 7.07-7.86 (m, 20H, Ar-H), 8.62 (s, 1H, NH); MS m/z (%): 466 (M^+, 48.6), 437 (19), 105 (33.2), 77 (100); Analysis for $C_{31}H_{22}N_4O$ (466.53): Calcd.: C, 79.81; H, 4.75; N, 12.01%; Found: C, 79.84; H, 4.77; N, 12.04%.

3-Benzoyl-4-phenyl-2-(phenylamino)pyrimido[1,2-*a*]benzimidazole (**9**); Yield 53%; m.p.249^{0}C (EtOH/DMF); IR (KBr) νmax/cm^{-1}: 3316 (NH), 1634 (C=O); ^{1}H NMR (DMSO-d_6):δ 6.34-8.76 (m, 19H, Ar-H); MS m/z (%): 440 (M^+, 14.22), 336 (58.1), 259 (22.24), 105 (16.99), 77 (100); Analysis for $C_{29}H_{20}N_4O$ (440.5): Calcd.: C, 79.07; H, 4.58; N, 12.72%; Found: C, 79.10; H, 4.56; N, 12.75%.

Reaction between of 2-[(methylsulfanyl)(phenyl amino)methylidene]-1,3-diphenylpropane-1,3-dione (3) and azoaminopyrazole derivatives

The typical running technique involves combining the proper pyrazole diazonium salt derivatives **10a-c** (2 mmol), chemical **3** (0.746 g, 2 mmol), ethanol (20 ml) and a few droplets of piperidine. This mixture is then refluxed for four hours and followed by cooling to atmospheric level. Once a precipitate has formed, the product is filtered out, cleaned using ethanol, and desiccated. The matching pyrazolo[1,5-*a*]pyrimidine derivatives **12a-c** were acquired through recrystallization from a compatible solvent.

6-Benzoyl-3-(2-phenyldiazenyl)-2-amino-7-phenyl-5-(phenylamino)pyrazolo[1,5-*a*]pyrimidine(**12a**): Yield 80%; m.p.198-200^{0}C (EtOH/DMF); IR (KBr) νmax/cm^{-1}: 3407, 3263 (NH_2), 3059 (NH), 1670 (C=O), ^{1}H NMR (DMSO-d_6):δ 3.57 (s, 2H, NH_2), 7.05-7.88 (m, 20H, Ar-H), 9.4 (s, 1H, NH); MS m/z (%): 509 (M^+, 2.74), 462 (14.17), 129 (26.63), 105 (64.32), 77 (100); Analysis for $C_{31}H_{23}N_7O$ (509.56): Calcd.: C, 73.07; H, 4.55; N, 19.24%; Found: C, 73.11; H, 4.58; N, 19.25%.

6-Benzoyl-3-(2-*p*-tolyldiazenyl)-2-amino-7-phenyl-5-(phenylamino)pyrazolo[1,5-*a*]pyrimidine(**12b**): Yield 83%; m.p.196^{0}C (EtOH/DMF); IR (KBr) νmax/cm^{-1}: 3403, 3263 (NH_2), 3138 (NH), 1665 (C=O); ^{1}H NMR (DMSO-d_6): δ 1.56 (s, 2H, NH_2), 2.37 (s, 3H, CH_3), 6.82-7.72 (m, 19H, Ar-H), 9.4 (s, 1H, NH).; MS m/z (%): 523 (M^+, 5.28), 289 (5.45), 222(6.49), 105 (100), 77 (80.48); Analysis for $C_{32}H_{25}N_7O$ (523.59): Calcd.: C, 73.41; H, 4.81; N, 18.73%; Found: C, 73.40; H, 4.84; N, 18.72%.

6-Benzoyl-3-(2-(4-chlorophenyl)diazenyl)-2-amino-7-phenyl-5-(phenylamino)pyrazolo[1,5-*a*]pyrimidine (**12c**): Yield 82%; m.p.248^{0}C (EtOH/DMF); IR (KBr) νmax/cm^{-1}: 3401, 3296 (NH_2), 3193 (NH), 1666 (C=O); ^{1}H NMR (DMSO-d_6):δ 5.96 (s, 2H, NH_2), 6.83-7.84 (m, 19H, Ar-H), 10.74 (s, 1H, NH); MS m/z (%): 546 (M^++2, 5.2), 545 (M^++1, 5.9), 544 (M^+, 6.5), 237 (6.5), 181 (7.89), 105 (96.1), 77 (100); Analysis for $C_{31}H_{22}N_7OCl$ (544.01): Calcd.: C, 68.44; H, 4.08; N, 18.02; Cl, 6.52%; Found: C, 68.46; H, 4.11; N, 18.05; Cl, 6.54%.

Interaction between 2-[(methylsulfanyl)(*N*-methylphenylamino)methylidene]-1,3-diphenylpropane-1,3-dione (4) and urea derivatives

After a 4-hour reflux period, a mixture of **4** (0.774 g, 2 mmol), either urea or thiourea (2 mmol), ethanol (20 ml), and a few drips of piperidine was allowed to cool down to a normal temperature. The resulting precipitate was extracted using a filter, rinsed with ethanol, and then evaporated. Components **13** and **14** were obtained, accordingly through recrystallization using the relevant solvent.

5-Benzoyl-4-(*N*-methyl-*N*-phenylamino)-2-hydroxy-6-phenylpyrimidine (**13**): Yield 85%; m.p.190^{o}C (EtOH/DMF); IR (KBr) νmax/cm^{-1}: 1656 (C=O); ^{1}H NMR (DMSO-d_6):δ 1.56 (s, 3H, CH_3), 5.38 (s,1H,OH), 6.82-7.58 (m, 15H, Ar-H); MS m/z (%): 381 (M^+, 2.7), 289 (2.7), 222 (3.3), 184 (3.9), 105 (70.6), 77 (100); Analysis for $C_{24}H_{19}N_3O_2$ (381.43): Calcd.: C, 75.57; H, 5.02; N, 11.02%; Found: C, 75.59; H, 5.05; N, 11.04%.

5-Benzoyl-6-(*N*-methyl-*N*-phenylamino)-1,2-dihydro-4-phenyl-2-thioxopyrimidine (**14**): Yield 90%; m.p.216-218^{0}C (EtOH/DMF); IR (KBr) νmax/cm^{-1}: 3137 NH, 1656 (C=O); ^{1}H NMR (DMSO-d_6):δ 1.56 (s, 3H, CH_3), 6.82-7.60 (m, 15H, Ar-H), 9.32 (s, 1H, NH); MS m/z (%): 397 (M^+, 2.4), 305 (9.41), 222

(5.9), 105 (100), 77 (63.7); Analysis for $C_{24}H_{19}N_3SO$ (397.49): Calcd.: C, 72.52; H, 4.82; N, 10.57; S, 8.07%; Found: C, 72.54; H, 4.85; N, 10.56; S, 8.09%.

Reaction of 2-[(methylsulfanyl)(*N*-methylphenyl amino)methylidene]-1,3-diphenylpropane-1,3-dione (4) with heterocyclic amines

Common practice

The proper heterocyclic amines, 2-aminopyridine (**15**) or 2-aminobenzothiazole (**16**) (2 mmol each), and ingredient **4** (0.774 g, 2 mmol) were combined with 15 ml of ethanol and a catalytic quantity of piperidine. The combination was then refluxed for four hours before being allowed to cool to standard ambient temperature. The resulting precipitate was filtered and cleaned with ethanol before being evaporated. The corresponding products **17** and **18** were obtained through recrystallization using a compatible solvent. Below is an inventory of **17** and **18**'s physical as well as spectral records:

3-(Methyl(phenyl)amino)-1-phenyl-2-benzoyl-3-(pyridin-2-ylamino)prop-2-en-1-one (**17**): Yield 80%; m.p.235-236ºC (EtOH/DMF); IR (KBr) νmax/cm^{-1}: 3435 (NH), 1660, 1639 (2C=O); ^{1}H NMR (DMSO-d_6): δ 2.07 (s, 3H, CH_3), 6.82-8.19 (m, 19H, Ar-H), 9.4 (s, 1H, NH); MS m/z (%): 433 (M^+, 10.8), 394 (22), 289 (18.4), 222(12.5), 105 (100), 77 (61.1); Analysis for $C_{28}H_{23}N_3O_2$ (433.50): Calcd.: C, 77.58; H, 5.35; N, 9.69%; Found: C, 77.54; H, 5.37; N, 9.72%.

3-(Methyl(phenyl)amino)-1-phenyl-2-benzoyl-3-(benzo- thiazol-2-ylamino)prop-2-en-1-one (**18**): Yield 78%; m.p.237-238ºC (EtOH/DMF); IR (KBr) νmax/cm^{-1}: 3431 (NH), 1660, 1639 (2C=O); ^{1}H NMR (DMSO-d_6):δ 2.07 (s, 3H, CH_3), 6.82-7.65 (m, 19H, Ar-H), 9.4 (s, 1H, NH); MS m/z (%): 489 (M^+, 3), 394 (7.2), 289 (8.3), 222(5.1), 105 (78.4), 77 (100); Analysis for $C_{30}H_{23}N_3SO_2$ (489.59): Calcd.: C, 73.60; H, 4.74; N, 8.58; S, 6.55%; Found: C, 73.58; H, 4.77; N, 8.61; S, 6.51%.

2.3.2. Reaction of 1,3-diphenylpropane-1,3-dione (1) with arylidenemalononitriles

General approach

Ammonium acetate (0.5 g) was added to a solution of 1,3-diphenylpropane-1,3-dione (**1**) (0.448 g, 2 mmol) and the relevant arylidenemalononitrile **19a-c** (2 mmol) in acetic acid. The reaction mixture was refluxed for 6 hours before being poured over crushed ice. After filtering, collecting, washing via water, drying, and recrystallizing the recovered precipitate using ethanol, we were able to generate the equivalent pyridine-3-carbonitrile derivatives **22a-c**.

4-(4-Chlorophenyl)-2-hydroxy-6-phenyl-5-(phenylcarbonyl)pyridine-3-carbonitrile (**22a**): Yield 76%; m.p.238ºC (EtOH/H_2O); IR (KBr) νmax/cm^{-1}: 2357 (C≡N), 1699 (C=O); ^{1}H NMR (DMSO-d_6):δ 6.20 (s, 1H, OH), 7.56-8.15 (m, 14H, Ar-H); MS m/z (%): 412 (M^++2, 15.3), 411 (M^++1, 10.2), 410 (M^+, 47.1), 116 (41.2), 76 (35.3), 56 (100); Analysis for $C_{25}H_{15}N_2O_2Cl$ (410.85): Calcd.: C, 73.08; H, 3.68; N, 6.82; Cl, 8.63%; Found: C, 73.10; H, 3.65; N, 6.84; Cl, 8.61%.

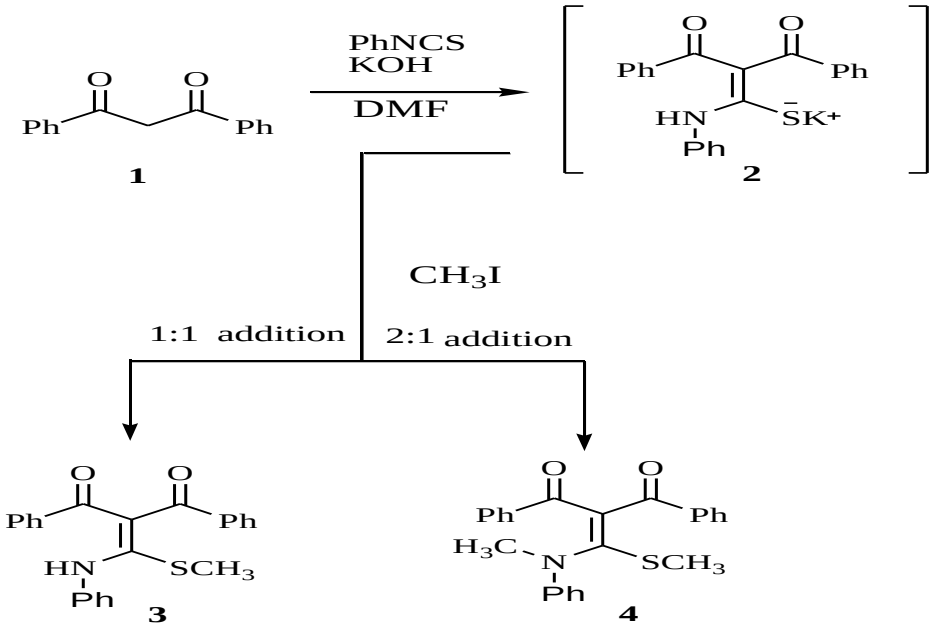
2-Hydroxy-6-phenyl-5-(phenylcarbonyl)-4-(thiophen-2- yl)pyridine-3-carbonitrile (**22b**): Yield 80%; m.p.98ºC (EtOH/H_2O); IR (KBr) νmax/cm^{-1}: 2362 (C≡N), 1638 (C=O); ^{1}H NMR (DMSO-d_6): δ 4.88 (s, 1H, OH), 7.33-8.19 (m, 13H, Ar-H); MS m/z (%): 382 (M^+, 1.7), 329 (3.3), 192 (100), 121 (28.3), 104

(7.5); Analysis for $C_{23}H_{14}N_2SO_2$ (382.44): Calcd.: C, 72.23; H, 3.69; N, 7.32; S, 8.38%; Found: C, 72.25; H, 3.72; N, 7.35; S, 8.36%.

4-(Furan-2-yl)-2-hydroxy-6-phenyl-5-(phenylcarbonyl)-pyridine-3-carbonitrile (**22c**): Yield 78%; m.p.75ºC (EtOH/H_2O); IR (KBr) νmax/cm^{-1}: 1966 (C≡N), 1634 (C=O); ^{1}H NMR (DMSO-d_6):δ 4.88 (s, 1H, OH), 7.34-8.19 (m, 13H, Ar-H); MS m/z (%): 366 (M^+, 25), 205 (30), 148 (70), 104 (80), 76 (100); Analysis for $C_{23}H_{14}N_2O_3$ (366.37): Calcd.: C, 75.40; H, 3.85; N, 7.65%; Found: C, 75.38; H, 3.87; N, 6.69%.

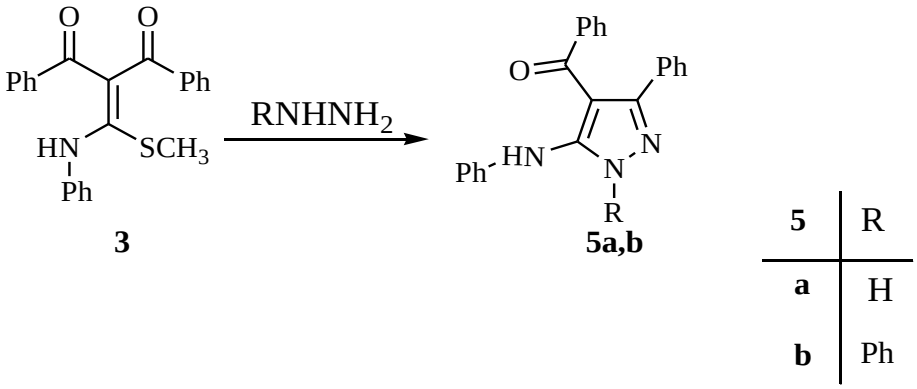
3. Results & Discussion

When 1,3-diphenylpropane-1,3-dione (**1**) was dissolved in dimethylformamide with phenyl isothiocyanate, potassium hydroxide was added, and the mixture was agitated at room temperature. After that, an equimolar amount of methyl iodide was added, resulting in a single product as confirmed by TLC analysis. This product was identified as 2-[(methylsulfanyl)(phenylamino)methylidene]-1,3-diphenylpropane-1,3-dione (**3**) through elemental studies.



Scheme 1

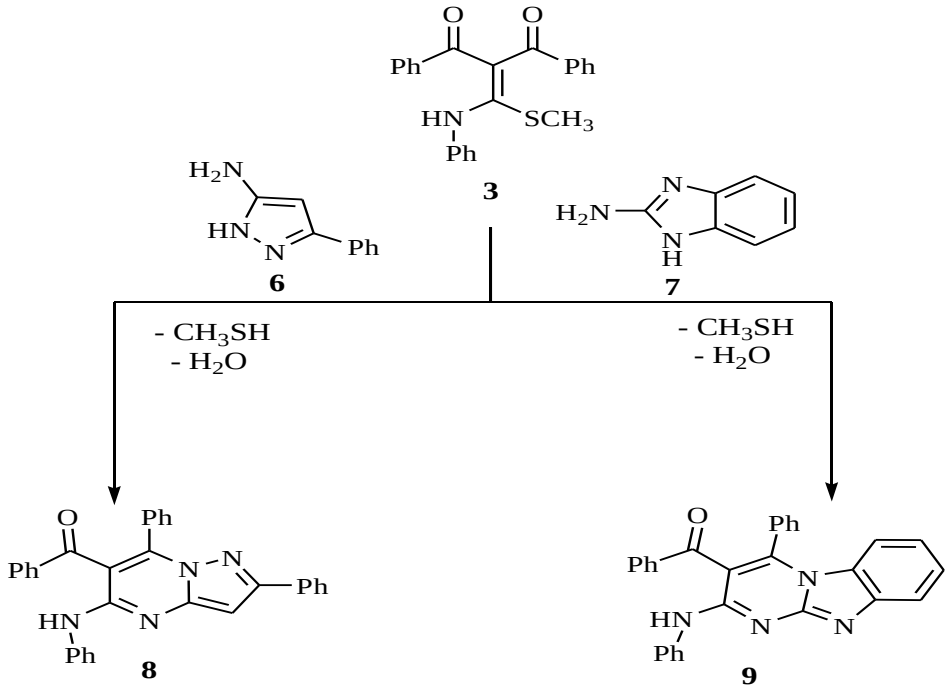
On the other hand, compound 2-[(methylsulfanyl)(*N*-methylphenylamino)methylidene]-1,3-diphenylpropane-1,3-dione (**4**) was synthesized by adding two equimolar equivalents of methyl iodide (Scheme 1). The ^{1}H NMR spectrum of the reaction product showed aromatic multiplet signals in the range of δ 7.03-8.19, as well as two singlet signals at δ 2.07 and 2.40, corresponding to S-CH_3 and N-CH_3 protons, respectively. Additionally, the mass spectrum displayed a peak at m/z 387, which was consistent with the molecular ion (see experimental section for details).



Scheme 2

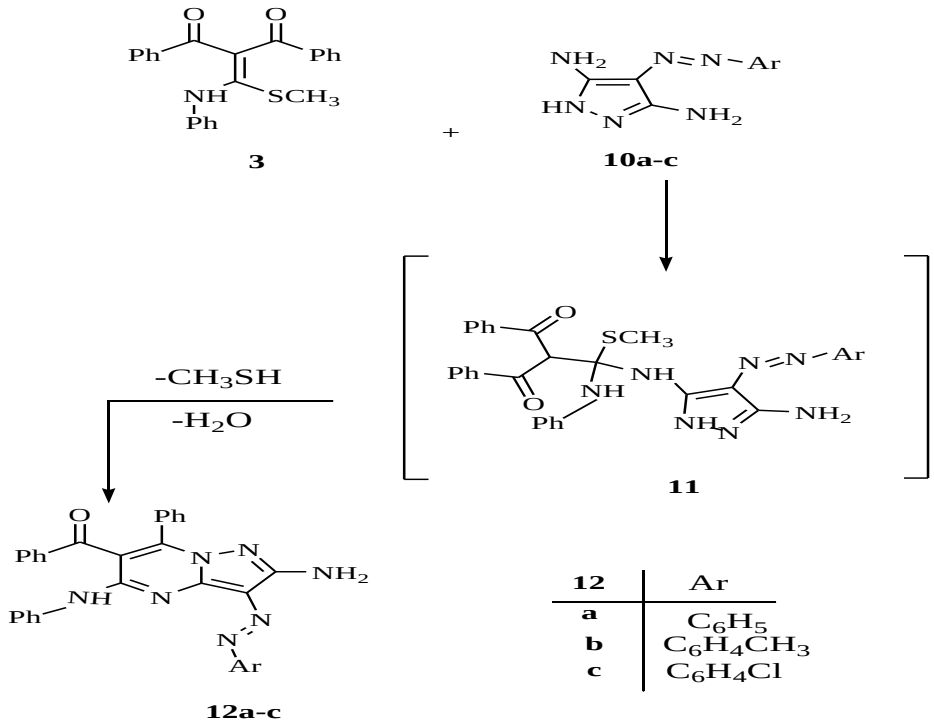
When chemical **3** was simmered with either hydrazine or phenylhydrazine in refluxing ethanol, it consistently produced a single, isolable product, in each instance. These products were identified as 4-benzoyl-3- phenyl-5-(phenylamino)-1*H*-pyrazole (**5a**) and 4- benzoyl-1,3-diphenyl-5-(phenylamino)-1*H*-pyrazole (**5b**), accordingly. (Scheme 2). Considering chemical **5a** as a prime instance, the infrared spectra showed one carbonyl absorption band and two NH bands at 1640, 3331, and 3169 cm^{-1}, sequentially. Further, the a molecular ion peak was visible in its mass spectrum at m/z 339.

Similarly, when combine **3** is reacted with 3-phenyl-5-amino-(1*H*)-pyrazole (**6**) and 2-aminobenzimidazole (**7**) in refluxing ethanol and with a catalytic portion of piperidine, it produces 2,7-diphenyl-5-(phenylamino)-6-benzoylpyrazolo[1,5-*a*]pyrimidine (**8**) and 3-benzoyl-4-phenyl-2-(phenylamino)pyrimido[1,2-*a*]benzimidazole (**9**) (Scheme 3). In both cases, a peak matching to the molecular ion was discernible in the mass profiles of the reaction products.



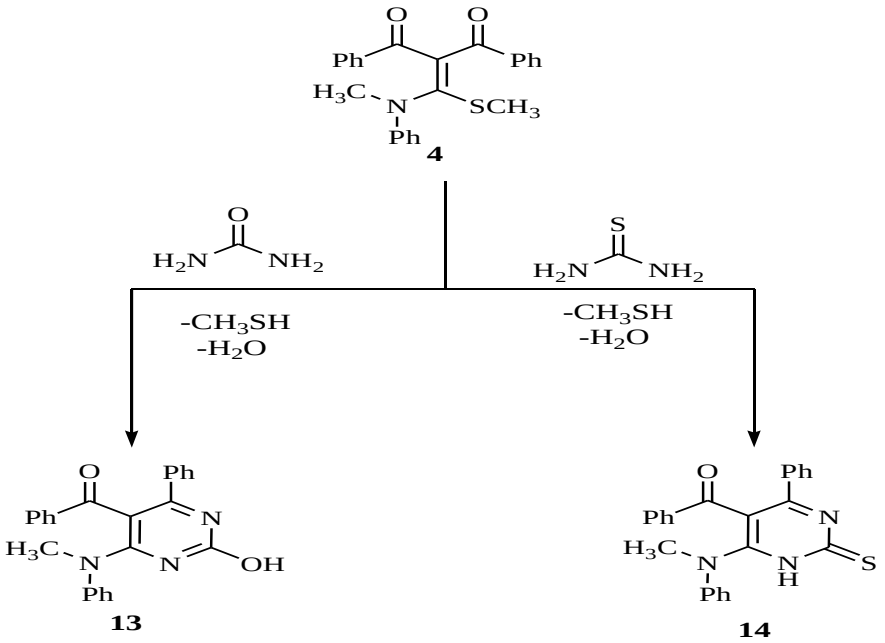
Scheme 3

In an identical way, substance **3** and its azoaminopyrazole derivatives (3-amino-4-arylhydrazono-5-imino-2-pyrazolines) **10a-c** reacted to generate 6-benzoyl-3-aryl-2-amino-7-phenyl-5-(phenylamino)-pyrazolo[1,5-*a*]pyrimidine **12a-c**, as illustrated in Scheme 4. The infrared spectra of ingredients **12a-c** each revealed the existence of two absorption bands for the NH_2 group in the range of 3263-3407 cm^{-1}, one absorption band for the NH function in the region 3059-3193 cm^{-1}, and one absorption band for carbonyls at 1667 cm^{-1}. Each time, a peak was identified as the molecular ion in the mass spectra. For instance, in the case of **12c**, the ^1H NMR spectrum exhibited two signals that were exchangeable with D_2O at δ 5.96 and 10.74, which were attributed to NH_2 and NH hydrogens, respectively, (refer to the experiment section for more details).



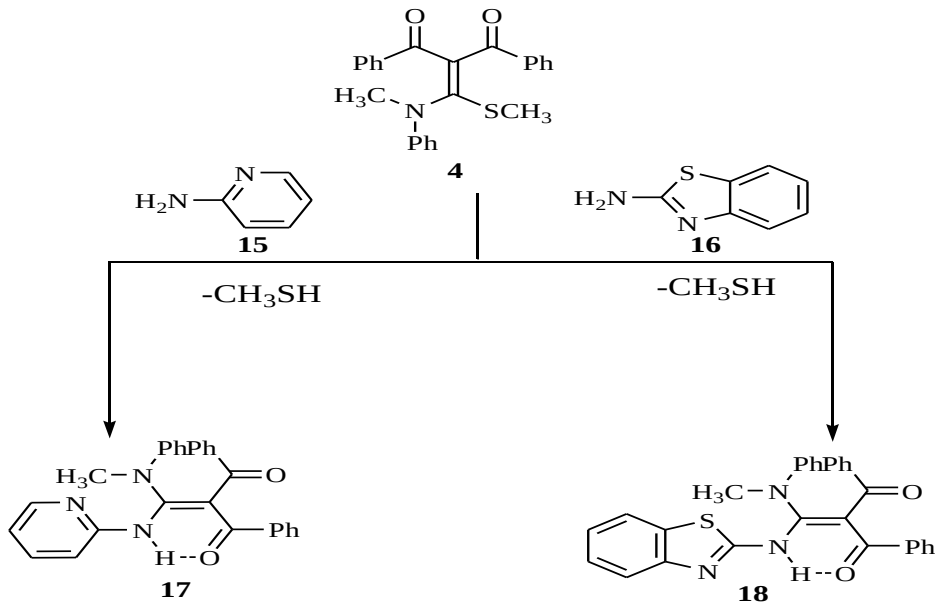
Scheme 4

The chemicals 5-benzoyl-4-(*N*-methyl-*N*-phenylamino)-2-hydroxy-6-phenylpyrimidine (**13**) and 5-benzoyl-6-(*N*-methyl-*N*-phenylamino)-1,2-dihydro-4-phenyl-2-thioxopyrimidine (**14**) were produced when compound **4** was combined with urea and thiourea in refluxing ethanol while a catalytic proportion of piperidine was present. Ingredient **13**'s infrared spectra indicated no NH stretching band and only one carbonyl absorption band at 1656 cm^{-1}. Furthermore, a D_2O exchangable signal at δ 5.38 in its ^1H NMR spectrum was found to be caused by an OH proton. However, the ^1H NMR spectra of compound **14** showed a D_2O exchangeable signal at δ 9.32, which can be attributed to the presence of an NH proton. Additionally, the IR spectrum of compound **14** displayed one NH absorption band at 3137 cm^{-1} and a carbonyl absorption band at 1656 cm^{-1}. Moreover, both compound **13** and compound **14**'s mass spectra exhibited a peak that matched the molecular ion (as shown in Scheme 5).



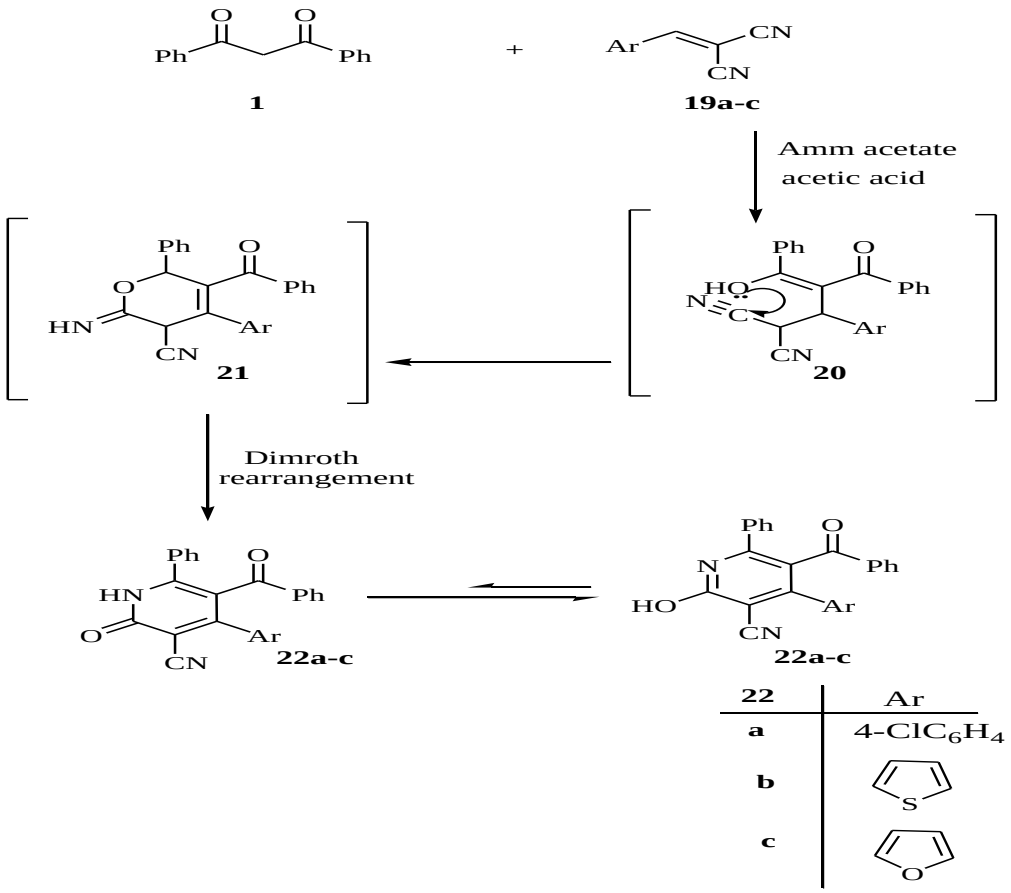
Scheme 5

Additionally, compound **4** was found to interact with 2-aminopyridine **15** and 2-aminobenzothiazole **16** under the identical circumstances, resulting in a single isolable product in each case, as confirmed by TLC analysis (see Scheme 6). The isolated products were identified as 3-(methyl(phenyl)amino)-1-phenyl-2-benzoyl-3-(pyridin-2-ylamino)prop-2-en-1-one (**17**) and 3-(methyl(phenyl)amino)-1-phenyl-2-benzoyl-3-(benzo- thiazol-2-ylamino)prop-2-en-1-one (**18**). The infrared spectra of the products showed one absorption band at 3433 cm^{-1}, which is characteristic of the NH function, and two carbonyl absorption bands at 1660 and 1639 cm^{-1} in each case. The ^{1}H NMR spectra of the products displayed two singlet signals at δ 2.07 and 9.4, respectively, caused by the CH_3 and NH protons. For further information, please refer to the experimental section.



Scheme 6

Furthermore, the response of 1,3-diphenylpropane-1,3-dione (**1**) towards various arylidenemalononitrile derivatives **19a–c** was assessed. This resulted in the formation of pyridine derivatives **22a-c** when compound **1** was reacted with arylidenemalononitriles **19a-c** under reflux conditions in the presence of acetic acid and ammonium acetate (Scheme 7). As an example of the synthesized series, compound **22a** displayed two distinct absorption bands in its infrared spectra at 2357 and 1699 cm^{-1}, corresponding to the nitrile and carbonyl groups, respectively. Furthermore, the mass spectrum revealed a fragment at m/z 410 that was attributed to a molecular ion, along with other pieces. The synthesis of the pyridine-3-carbonitrile derivatives **22a-c** is proposed to involve the iminopyrane adduct **21**, followed by a Dimroth-type rearrangement. Scheme 7 outlines a feasible methodology for the synthesis of these derivatives.



Scheme 7

4. Conclusion:

According to the study's findings, 1,3-diphenylpropane-1,3-dione (**1**) can be used to synthesize novel heterocyclic molecules. One method to achieve this is by reacting 1,3-diphenylpropane-1,3-dione (**1**) with phenyl isothiocyanate in dimethylformamide, while adding potassium hydroxide and an equimolar amount of methyl iodide. This reaction will result in the formation of 2-[(methylsulfanyl)(phenylamino)methylidene]-1,3-diphenylpropane-1,3-dione (**3**). While adding, two equimolar equivalents of methyl iodide were used to create 2-[(methylsulfanyl)(*N*-

methylphenylamino)methylidene]-1,3-diphenylpropane-1,3-dione (**4**), and by employing these synthesized materials in later reactions, new compounds were created. All generated products' structures were clarified using elemental analysis, mass spectroscopy, ^{1}H-NMR, and infrared spectroscopy.

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