Turkish Journal of Chemistry
http://journals.tubitak.gov.tr/chem/
Research Article

Turk J Chem
(2013) 37: 610 – 618

doi:10.3906/kim-1303-90

Synthesis of fused tetrazolone derivatives

Sevil ÖZCAN,[1] **Zeynep EKMEKÇİ,**[1,2] **Berk MÜJDE,**[1] **Metin BALCI**[1,*]
[1]Department of Chemistry, Middle East Technical University, Ankara, Turkey
[2]Department of Chemistry, Süleyman Demirel University, Isparta, Turkey

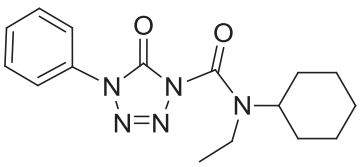
Received: 27.03.2013 • **Accepted:** 10.05.2013 • **Published Online:** 12.07.2013 • **Printed:** 05.08.2013

Abstract: New fused tetrazolone derivatives were synthesized using homophthalic and maleic anhydrides. Treatment of anhydrides with trimethylsilyl azide opened the lactone rings and formed the corresponding intermediates, which bore 1,3-dipole and dipolarophile functionalities in *ortho* positions. The intermediates partially underwent internal 1,3-dipolar cycloaddition to produce fused tetrazolone derivatives. When the carbonyl groups in anhydride were not conjugated with any double bond, then a triazine-fused tetrazolone derivative was formed.

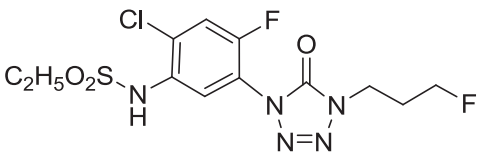
Key words: Tetrazolone, acyl azide, Curtius rearrangement, 1,3-dipole, dipolarophile, 1,3-dipolar cycloaddition

1. Introduction

Heterocyclic compounds display a broad spectrum of biological activities. Among the nitrogen-containing heterocycles, tetrazolones[1] have attracted considerable attention due to their excellent herbicidal activity.[2,3] One of the best known tetrazolone derivatives as a commercial herbicide is fentrazamide (**1**), which is highly effective against many weeds and inhibits cell division.[4] Another important example of tetrazolones is 1-aryl-4-(3-fluoropropyl)-tetrazolone (**2**), which was developed as a new and highly active family of protoporphyrinogen oxidase-inhibiting herbicides.[5]



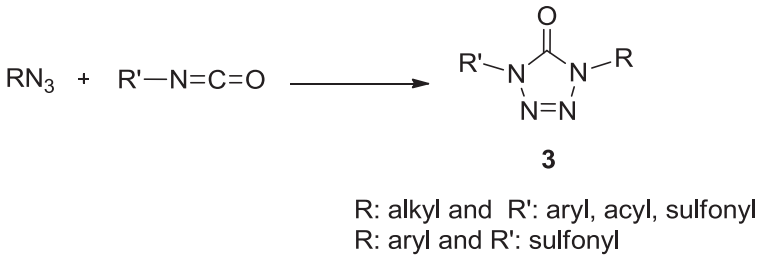
1



2

The tetrazolone scaffold is especially important for pesticide development and the most general synthetic approach for tetrazolone synthesis involves 1,3-dipolar cycloaddition reaction of azides to isocyanates (Scheme 1).

*Correspondence: mbalci@metu.edu.tr
In memory of Prof Dr Ayhan S. Demir

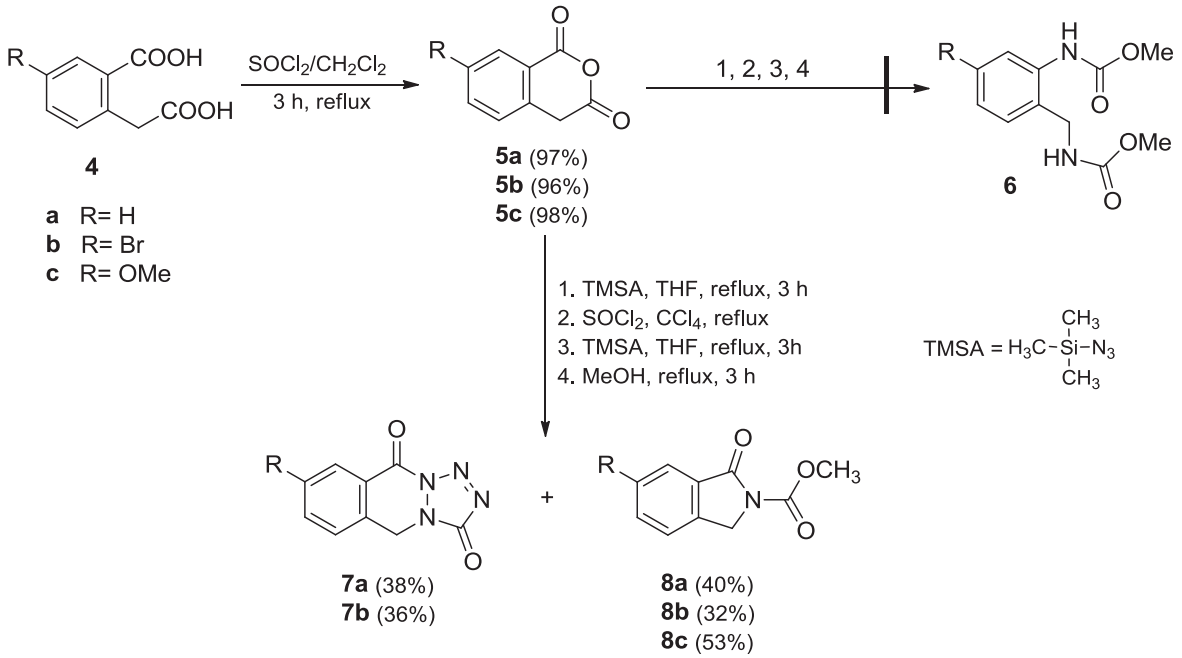


Scheme 1. The synthesis of 1,4-disubstituted tetrazolone.

The reaction of aryl isocyanates with either sodium azide or aluminum azide to form tetrazolones has long been known in the literature.[6–8] Trimethylsilyl azide (TMSA), in analogy with azides, also behaves as a 1,3-dipole towards isocyanates to synthesize tetrazolones.[9,10] For example, 1.3-dipolar cycloaddition of phenyl isocyanate to excess of TMSA has been reported to afford the corresponding tetrazolone derivative.[10] As an alternative to TMSA, Salama et al. have recently reported an inexpensive, in situ generated $SiCl_4/NaN_3$ combination that can be used as 1,3-dipole towards isocyanates to produce tetrazolones.[11] In the literature, there is a continuous focus on 1- and 4-substituted tetrazolone derivatives, which have been proved to show important herbicidal activities.[2–5] To the best of our knowledge, the synthesis or herbicidal activity of fused tetrazolones has not been reported yet. Herein, we report a simple, mild, and one-pot synthesis of novel fused tetrazolone derivatives starting from anhydrides.

2. Results and discussion

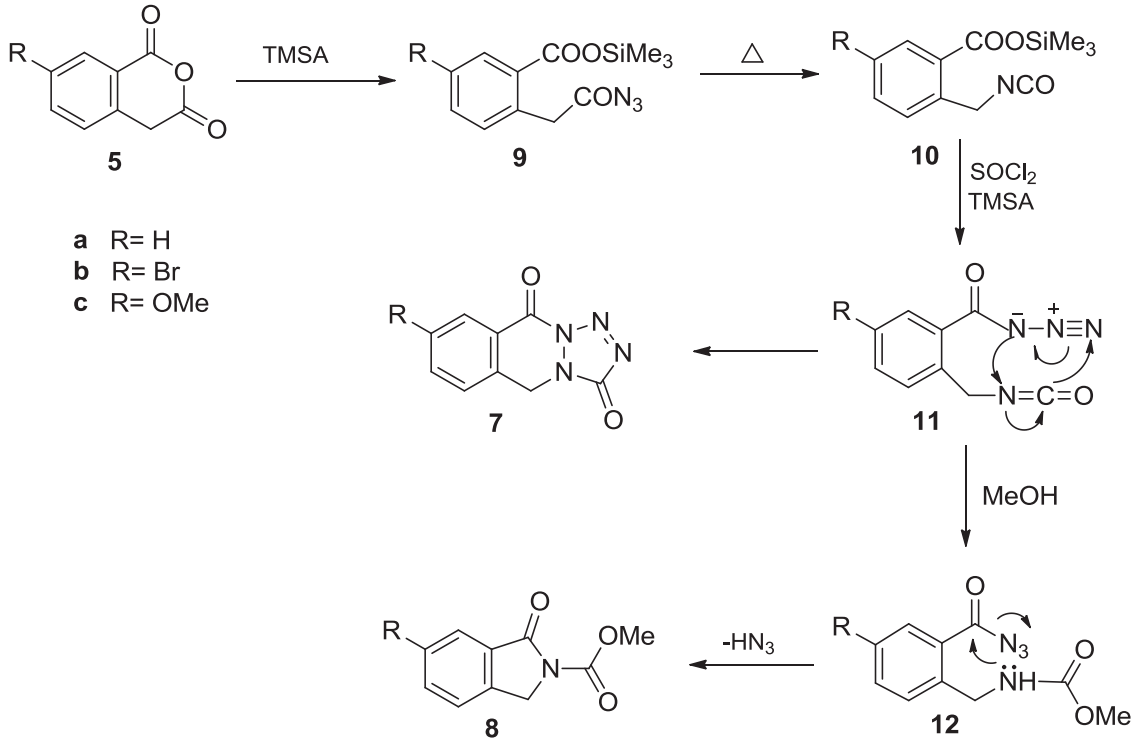
Our primary goal was the synthesis of **6**, which is an important precursor to undergo further cyclization reactions to produce heterocyclic compounds. As the starting material, homophthalic acid and its derivatives were used.



Scheme 2. Synthesis of fused tetrazolone derivatives **7** starting from the substituted homophthalic acids **4**.

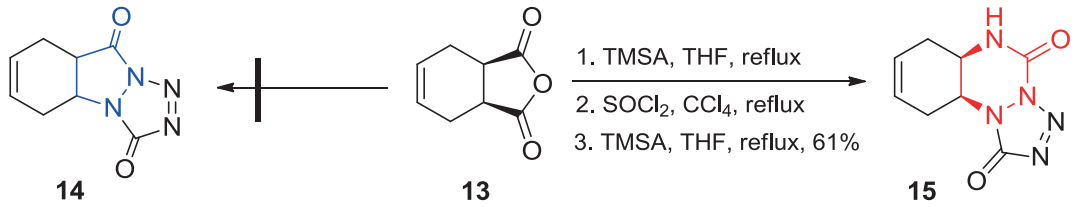
Bromo and methoxy homophthalic acids **4b** and **4c** were synthesized using the protocols reported in one of our recent studies.[12] For the synthesis of **5**, the acids were treated with thionyl chloride in dichloromethane and the corresponding anhydrides **5**[13] were obtained in high yields. The anhydride **5a–c** were reacted with TMSA and thionyl chloride, followed by a second molar equivalent of TMSA and methanol, respectively, as shown in Scheme 2. Analysis of the products indicated the formation of tetrazolones (**7a–b**) in 36%–38% yields and isoindolinones (**8a–c**) in 32%–53% yields instead of the expected product **6**. This result was not that surprising since the intermediates formed during this reaction have the potential to form isocyanate as dipolarophile and acyl azide as 1,3-dipole to undergo a 1,3-dipolar cycloaddition reaction.

The suggested mechanism for the formation of **7a–b** and **8a–c** is shown in Scheme 3. Under the reaction conditions, the lactones **5** first undergo ring opening reaction with TMSA to form intermediates **9a–c**. Under the refluxing conditions, Curtius rearrangement takes place and forms the intermediates **10a–c**. Subsequent addition of thionyl chloride followed by second molar equivalent of TMSA converts trimethylsilyl esters **10** into acyl azide intermediates **11**, which bear 1,3-dipole and dipolarophile functionalities in *ortho* positions. The intermediates **11a–b** partially undergo internal 1,3-dipolar cycloaddition to produce fused tetrazolone derivatives **7a–b**. Moreover, isocyanate is partially trapped with methanol to form the intermediates **12a–c**. The attack of lone pairs on urethane NH on the azide carbonyl results in the formation of isoindolinones **8a–c**. Methoxy substituted anhydride **5c** only produces isoindolinone derivative **8c**, favoring the intermediate **12c**.



Scheme 3. Suggested mechanism for the formation of **7a–b** and **8a–c**.

In order to test the effect of the benzene ring on the mode of this reaction, we first synthesized the anhydride **13**[14] by the addition of maleic anhydride to in situ generated butadiene. The anhydride **13** was treated with TMSA under the same reactions conditions as described above. However, the reaction produced **15** instead of the expected product **14.**



Scheme 4. Synthesis of a 1,2,4-trazinan-3-one fused tetrazolone derivative **15**.

The tetrazolone derivative **15** was characterized by spectral methods. The number of nitrogen atoms was determined by elemental analysis. According to the results of HRMS and elemental analysis, compound **15** contains 5 nitrogen atoms. The NH proton was observed at 7.62 ppm as a singlet. The ^{13}C NMR revealed the presence of 2 carbonyl carbon atoms resonating at 153.9 and 153.5 ppm, indicating the connection to 2 nitrogen atoms from both sides of the carbonyl groups. In the HMBC spectrum (Figure 1), carbonyl carbon resonances correlate with the proton resonances appearing at 4.37 (H_{10a}) and 3.97 (H_{7a}) as well as with the NH proton resonating at 7.62 ppm. These correlations support the exact positions of the carbonyl groups.

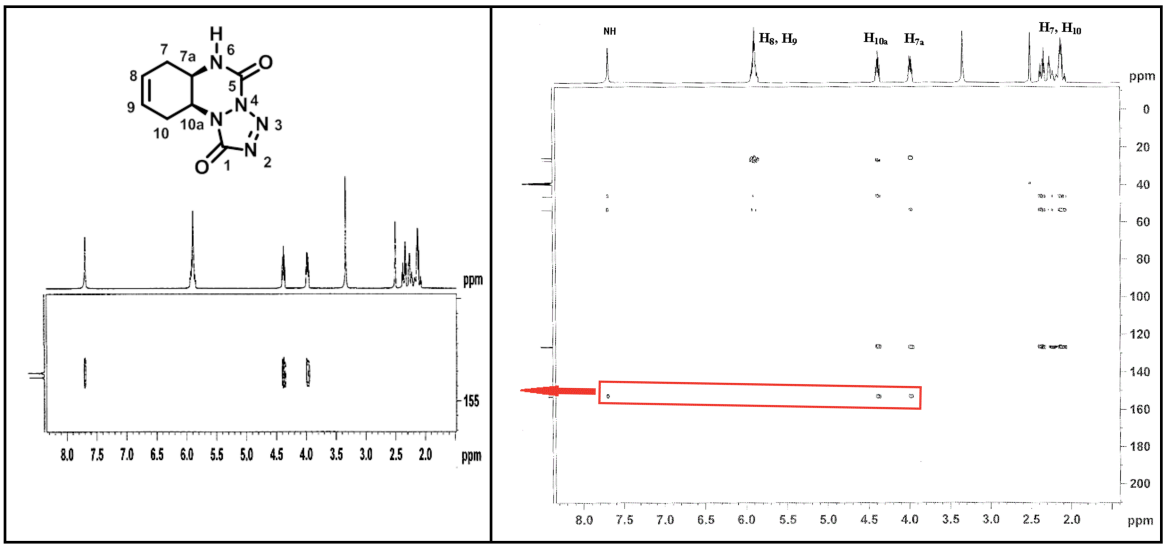
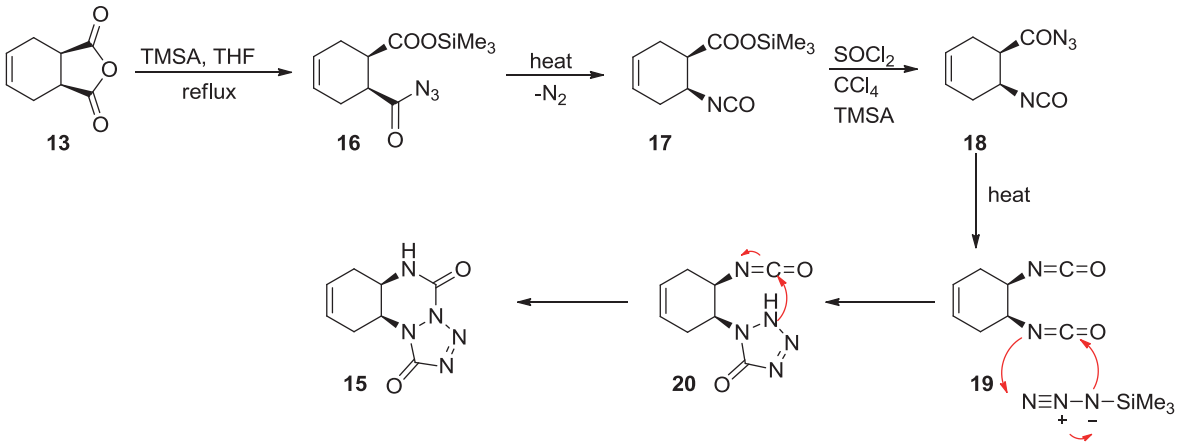


Figure. HMBC spectrum of compound **15**.

The following mechanism was suggested for the formation of the product **15** (Scheme 5). The anhydride **13** first undergoes a ring opening reaction with TMSA to form the intermediate **16**. Then the acyl azide functionality in **16** rearranges to the isocyanate **17**. Reaction of **17** with thionyl chloride followed by a second molar equivalent of TMSA converts trimethylsilyl ester into acyl azide **18**, which prefers the rearrangement to the corresponding bisisocyanate **19** instead of intramolecular addition to the isocyanate group to give **14**. Bisisocyanate **19** reacts with TMSA to form the intermediate **20**, which then undergoes an internal addition reaction to produce fused tetrazolone derivatives **15.**

Our experimental results allow us to conclude that under the same reaction conditions anhydrides **5** and **13** show different reactivity. In the case of **5**, there are 2 different acyl azide functionalities, with one of the carbonyl groups conjugated with the benzene ring and the other one not. Recently, we showed that the stability of those acyl azides is different and the conjugated one is more stable than the other.[15] However, in the case of **13**, neither of the acyl azide functions is in conjugation with any other groups so that neither of them will

be as stable as the conjugated one and they will be expected to undergo Curtius rearrangement much faster. However, one of the acyl azide groups generated from **5** is stabilized due to the conjugation with the benzene ring and therefore prefers addition to the isocyanate group over rearrangement. As a result of this reactivity difference, the formed products starting from **5** and **13** are different.



Scheme 5. Suggested mechanism for the formation of **15**.

In conclusion, we developed a new practical and efficient route to novel fused tetrazolone as well as to isoindolinone derivatives starting from cheap and readily available reagents such as homophthalic acid derivatives and maleic anhydride. The mild reaction conditions, easy work-up procedure, and simple operation are advantages of this procedure.

3. Experimental section

3.1. General

Melting points were determined on a Thomas-Hoover capillary melting point apparatus. IR spectra were recorded on a PerkinElmer 980 spectrometer. NMR spectra were recorded on a Bruker-Avance instrument at 400 MHz for ^{1}H and 100 MHz for ^{13}C NMR. Apparent splitting is given in all cases. Column chromatography was performed on silica gel (60-mesh, Merck). TLC was carried out on Merck 0.2 mm silica gel 60 F_{254} analytical aluminum plates. Elemental analyses were carried out on a Leco-932 model CHNS analyzer.

3.2. Isochroman-1,3-dione (5a)

To a stirred solution of homophthalic acid (5.0 g, 27.8 mmol) in dichloromethane (100 mL) was added an excess amount of thionyl chloride (5 mL, 68 mmol). The reaction mixture was refluxed until a clear solution was formed (3 h). After the completion of the reaction, the solvent and excess thionyl chloride were evaporated under reduced pressure to obtain **5a** (4.4 g, 97%) as a yellow solid, mp 143–144 °C (Lit. 144–145 °C[16]). ^{1}H NMR (400 MHz, $CDCl_3$)δ 8.22 (br d, $J_{9,10}$ = 7.8 Hz, 1H, H-10), 7.70 (br dd, $J_{9,10}$ = 7.8 Hz, $J_{8,9}$ = 7.6 Hz, 1H, H-9), 7.52 (br t, $J_{8,9}$ = $J_{7,8}$ = 7.6 Hz, 1H, H-8), 7.35 (br d, $J_{7,8}$ = 7.6 Hz, 1H, H-7), 4.14 (s, 2H, H-3); ^{13}C NMR (100 MHz, $CDCl_3$)δ 165.0, 161.3, 135.9, 134.7, 131.3, 129.1, 127.9, 121.9, 34.7; Anal. Calcd for $C_9H_6O_3$: C, 66.67; H, 3.73. Found: C, 66.48; H, 4.06.

3.3. 7-Bromoisochroman-1,3-dione (5b)[17,18]

The same procedure for **5a** was followed except using 5-bromo-2-(carboxymethyl)benzoic acid **(4b)** (5.0 g, 19 mmol) and thionyl chloride (5 mL, 68 mmol). The product **5b** (4.5 g, 18.6 mmol, 98%) was obtained as a pale yellow solid, mp 171–173 °C. ^{1}H NMR (400 MHz, $CDCl_3$)δ 8.26 (br s, 1H, H-10), 7.73 (br dd, $J_{8,7}$ = 8.2 Hz, $J_{8,10}$ = 1.6 Hz, 1H, H-8), 7.16 (br d, $J_{7,8}$ = 8.2 Hz, 1H, H-7), 4.02 (s, 2H, H-3); ^{13}C NMR (100 MHz, $CDCl_3$)δ 161.2, 157.2, 136.0, 131.1, 130.5, 126.6, 120.9, 120.1, 31.6; IR (KBr, cm^{-1}) 3094, 2949, 1796, 1780, 1296, 1195, 1177, 1060, 906, 762, 727; Anal. Calcd. for $C_9H_5BrO_3$; C, 44.85; H, 2.09; Br, 33.15 Found: C, 44.69; H, 2.20.

3.4. 7-Methoxyisochroman-1,3-dione (5c)[18]

The same procedure for **5a** was followed except using 2-(carboxymethyl)-5-methoxybenzoic acid (5.0 g, 23.7 mmol) and thionyl chloride (5 mL, 68 mmol). The product **5c** (4.4 g, 96%) was obtained as a pale yellow solid, mp 180–182 °C. ^{1}H NMR (400 MHz, $CDCl_3$)δ 7.58 (d, $J_{10,8}$ = 2.0 Hz, 1H, H-10), 7.19–7.17 (m, 2H, H-8 and H-7), 4.01 (s, 2H, H-3), 3.82 (s, 3H, -OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$)δ 164.9, 161.2, 159.9, 128.8, 126.6, 124.2, 122.7, 113.2, 56.0, 34.0.

3.5. Synthesis of 3*H*-tetrazolo[2,1-*b*]phthalazine-3,10(*5H*)-dione (7a) and methyl 1-oxoisoindoline-2-carboxylate (8a)

To a stirred solution of homophthalic anhydride **(5a)** (1.05 g, 6.5 mmol) in THF (25 mL) was added 1.2 equivalent of trimethylsilyl azide (TMSA) (1.02 mL, 7.8 mmol), followed by refluxing for 3 h. THF was evaporated and the residue was dissolved in CCl_4 (25 mL) and to this mixture was added thionyl chloride (0.53 mL, 7.8 mmol). The resulting mixture was refluxed for 3 h and the solvent was evaporated and the remaining residue was dissolved in THF (25 mL) and to this mixture was added a second molar equivalent of TMSA (1.02 mL, 7.8 mmol). After 3 h of refluxing the solvent was removed and the residue was dissolved in methanol (25 mL) and further refluxed for 3 h. Methanol was evaporated and the residue was chromatographed on silica gel (40 g) eluting with EtOAc/hexane (3/2) to give the compounds **7a** (0.5 g, 38%) and **8a** (0.5 g, 40%). The obtained products were further purified by recrystallization from EtOAc/hexane (5:1). **3*H*-Tetrazolo[2,1-*b*]phthalazine-3,10(5*H*)-dione (7a)**. Pale yellow solid, mp 281–283 °C. ^{1}H NMR (400 MHz, $CDCl_3$)δ 7.86 (d, $J_{10,11}$ = 7.5 Hz, 1H, H-10), 7.63 (t, $J_{10,11}$ = $J_{11,12}$ = 7.5 Hz, 1H, H-11), 7.46 (m, 2H, H-12, H-13), 4.39 (s, 2H, H-9); ^{13}C NMR (100 MHz, $CDCl_3$)δ 165.6, 154.4, 140.7, 134.3, 130.4, 128.9, 125.5, 123.3, 49.2; IR (KBr, cm^{-1}) 2251, 1744, 1695, 1363, 1337, 1282, 1213, 1194, 1158, 722, 554; Anal. Calcd. for $C_9H_6N_4O_2$: C, 53.47; H, 2.99; N, 27.71 Found: C, 53.21; H, 3.38; N, 27.49.

Methyl 1-oxoisoindoline-2-carboxylate (8a).[19] White solid, mp 143–147 °C. ^{1}H NMR (400 MHz, $CDCl_3$)δ 7.78 (d, $J_{8,9}$ = 7.5 Hz, 1H, H-9), 7.57 (t, $J_{7,8}$ = $J_{8,9}$ = 7.5 Hz, 1H, H-8), 7.46 (d, $J_{6,7}$ = 7.5 Hz, 1H, H-6) 7.42 (t, $J_{6,7}$ = $J_{7,8}$ = 7.5 Hz, 1H, H-7), 4.72 (s, 2H, H-2), 3.85 (s, 3H, -OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$)δ 171.4, 157.4, 146.4, 138.9, 136.1, 133.7, 129.9, 128.5, 58.5, 54.3; IR (KBr, cm^{-1}) 2956, 2251, 1785, 1598, 1469, 1263, 1190, 1103, 1019, 999, 884, 771, 681, 581, 479; Anal. Calcd. for $C_{10}H_9NO_3$: C, 62.82; H, 4.74; N, 7.33 Found: C, 62.51; H, 4.48; N, 7.70.

3.6. Synthesis of 7-bromo-3*H*-tetrazolo[2,1-*b*]phthalazine-3,10(*5H*)-dione (7b) and methyl 6-bromo-1-oxoisoindoline-2-carboxylate (8b)

The same procedure for **7a** and **8a** was followed except using 7-bromoisochroman-1,3-dione **(5b)** (1.56 g, 6.5 mmol), TMSA (1.02 mL, 7.8 mmol), thionyl chloride (1.6 mL, 23.4 mmol), and TMSA (1.02 mL, 7.8 mmol). The products were chromatographed on silica gel (40 g) eluting with EtOAc/hexane (3/2) to give compounds **7b** (0.65 g, 36%) and **8b** (0.56 g, 32%).

7-Bromo-3*H*-tetrazolo[2,1-*b*]phthalazine-3,10(5H)-dione (7b). ^{1}H NMR (400 MHz, $CDCl_3$)δ 8.0 (d, $J_{10,12}$ = 2.0 Hz, 1H, H-10), 7.73 (dd, $J_{12,10}$ = 2.0 Hz, $J_{12,13}$ = 6.2 Hz, 1H, H-12), 7.33 (d, $J_{13,12}$ = 6.2 Hz, 1H, H-13), 4.74 (s, 2H, H-9a,b); ^{13}C NMR (100 MHz, $CDCl_3$)δ: 164.5, 154.7, 139.5, 137.7, 132.7, 128.8, 135.3, 132.2, 49.3; IR (KBr, cm^{-1}) 2957, 2260, 2160, 1799, 1758, 1757, 1325, 1251, 1145, 1057, 1026, 913, 842, 736.

Methyl 6-bromo-1-oxoisoindoline-2-carboxylate (8b).[19b] Pale yellow solid, mp 186–188 °C. ^{1}H NMR (400 MHz, $CDCl_3$)δ: 8.1 (d, $J_{7,9}$ = 2.0 Hz, 1H, H-9), 7.77 (dd, $J_{7,9}$ = 2.0 Hz, $J_{6,7}$ = 6.2 Hz, 1H, H-7), 7.38 (d, $J_{6,7}$ = 6.2 Hz, 1H, H-6), 4.80 (s, 2H, H-2a,b), 3.99 (s, 3H, -OCH3); ^{13}C NMR (100 MHz, $CDCl_3$)δ: 165.0, 153.6, 139.6, 137.1, 133.3, 128.6, 125.1, 123.6, 54.2, 49.2; IR (KBr, cm^{-1}) 3058, 3007, 2949, 2848, 1767, 1695, 1438, 1363, 1320, 1256, 1208, 1139, 1005, 886, 848.

3.7. Synthesis of methyl 6-methoxy-1-oxoisoindoline-2-carboxylate (8c)

The same procedure for **7a** and **8a** was followed except using 7-methoxyisochroman-1,3-dione **(5c)** (1.25 g, 6.5 mmol), TMSA (1.02 mL, 7.8 mmol), thionyl chloride (0.53 mL, 7.8 mmol), and TMSA (1.02 mL, 7.8 mmol). The residue was chromatographed on silica gel (40 g) eluting with EtOAc/hexane (3/2) to obtain compound **8c** (0.76 g, 53%) as a single product.

Methyl 6-methoxy-1-oxoisoindoline-2-carboxylate (7c).[19b] ^{1}H NMR (400 MHz, $CDCl_3$)δ 7.63 (d, $J_{7,9}$ = 2.8 Hz, 1H, H-9), 7.19 (d, $J_{6,7}$ = 8.4 Hz, 1H, H-6), 7.07 (dd, $J_{6,7}$ = 8.4 Hz, $J_{7,9}$ = 2.8 Hz, 1H, H-7), 3.99 (s, 2H, H-2a,b), 3.86 (s, 3H, -OCH_3), 3.70 (s, 3H, -OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$)δ: 164.8, 158.7, 139.4, 133.5, 128.8, 125.1, 119.7 116.5, 55.5, 51.9, 39.8.

3.8. Synthesis of 6a,7,10,10a-tetrahydro-1*H*-tetraazolo[1,2-*a*][1,2,4]benzotri-azine-1,5(6*H*)-dione (15)

To a stirred solution of 1,2,3,6-tetrahydrophthalic anhydride (**13**) (1.0 g, 6.6 mmol) in THF (40 mL) was added TMSA (1.06 g, 9.2 mmol) and the solution was heated to reflux temperature. N_2 evolution was over after 30–45 min. The solution was cooled and concentrated in vacuum. The residue was dissolved in CCl_4 (20 mL) and to this solution was added DMF (3 drops) followed by $SOCl_2$ (0.347 g, 2.92 mmol). The reaction mixture was heated to 40–50 °C. The reaction was monitored by IR. When the infrared absorption at 1720 cm^{-1} (ester) disappeared (30–45 min), the solution was cooled to room temperature and concentrated in vacuum (bath temperature should be below 35 °C). The remaining residue was dissolved in THF (25 mL) and to this solution was added TMSA (1.06 g, 9.02 mmol) at r.t., which was subsequently heated to 80–85 °C for 90 min. After the reaction was completed, the solution was cooled to room temperature. Brown precipitate was filtered and washed with CH_2Cl_2 and the residue was crystallized from hot ethanol to give product **15** (1.15 g, 61%) as colorless crystals, mp 143–144 °C. ^{1}H NMR (400 MHz, DMSO-d_6)δ 7.62 ppm (s, 1H, -NH-), 5.85–5.80 (m,

2H, H_8 and H_9), 4.37 (q, J = 4.6 Hz, 1H, H_{10a}), 3.97 (q, J = 4.1 Hz, 1H, H_{7a}), 2.36 (dd, J = 15.6 and J = 4.4 Hz, 1H), 2.24 (m, 1H), 2.20–2.06 (m, 2H); ^{13}C NMR (100 MHz, DMSO, ppm) δ 153.9, 153.5, 127.6, 127.3, 54.2, 46.9, 28.1, 26.5; IR (KBr, cm^{-1}) 3344, 3316, 3043, 2970, 2171, 2152, 1751,176, 1340, 1179, 627; Anal. Calcd. for $C_8H_9N_5O_2$: C, 46.38; H, 4.38; N, 33.80 Found: C, 46.41; H, 4.36; N: 34,19; HRMS: Anal. Calcd. for $C_8H_9N_5O_2$ $[M+H]^+$: 208.0829. Found $[M+H]^+$: 208.0879.

Acknowledgments

The authors are indebted to the Scientific and Technological Research Council of Turkey (TÜBİTAK, Grant Nos 108-M-168 and TBAG-110 R 001), the Department of Chemistry at Middle East Technical University, and the Turkish Academy of Sciences (TÜBA) for their financial support of this work.

References

1. (a) Nagendra, G.; Narendra, N.; Sureshbabu, Vommina V. *Indian J. Chem. Section B.* **2012**, *51B*, 486–492; (b) Bahadoor, A.; Castro, A. C.; Chan, L. K.; Keaney, G. F.; Nevalainen, M.; Nevalainen, V.; Peluso, S.; Snyder, D. A.; Tibbitts, T. T. PCT Int. Appl. **2011**, WO 2011140190 A1 20111110; (c) Alawode, O. E.; Robinson, C.; Rayat, S. *J. Org. Chem.* **2011**, *76,* 216–222; (d) Gundugola, A. S.; Chandra, K. L.; Perchellet, E. M.; Waters, A. M.; Perchellet, J.-P. H.; Rayat, S. *Bioorg. Med. Chem.* **2010**, *20,* 3920–3924; (e) Zarubaev, V. V.; Golod, E. L.; Anfimov, P. M.; Shtro, A. A.; Saraev, V. V.; Gavrilov, A. S.; Logvinov, A. V.; Kiselev, O. I. *Bioorg. Med. Chem.* **2010**, *18*, 839–848; (f) Logvinov, A. V.; Polyakova, I. N.; Golod, E. L. *Rus. J. Gen. Chem.* **2009**, *79*, 2220–2229; (g) Holt, J.; Fiksdahl, A. *J. Heterocycl. Chem.* **2007**, *44,* 375–379; (h) Egorova, N. G.; Artamonova, T. V.; Hrabalek, A.; Koldobskii, G. I. *Rus. J. Org. Chem.* **2005**, *41,* 1399–1401.
2. Luo, Y-P.; Lin, L.; Yang, G.-F. *J. Heterocycl. Chem.* **2007**, *44*, 937–943.
3. (a) Kathleen, M. P.; Lawrenceville, N. J. US Patent, 4,913,724, **1990**; (b) Yanagi, A.; Watanabe, Y.; Narabu, S. US Patent, 5,530,135, **1996**.
4. (a) Goto, T.; Ito, S.; Yanagi, A.; Watanabe, Y.; Yasui, K. *Weed. Biol. Manag.* **2002**, *2*, 18–24. (b) Y.-P. L.; Guang-Fu. Y. *Bioorg. Med. Chem.* **2007**, *15*, 1716–1724.
5. (a) Theodoridis, G.; Hotzman, F. W.; Scherer, L. W.; Smith, B. A.; Tymonko, J. M.; Wyle, M. J. *Pestic. Sci.* **1990**, *30*, 259–274. (b) Theodororidis, G. PCT Int. Appl. WO 85 01, 939 (CI.C07D257/04); Chem. Abstr. 103 (**1985**) 141977f.
6. Horwitz, J. P.; Fisher B. E.; Tomazevski, A. J. *J. Am. Chem. Soc.* **1959**, *81*, 3076–3079.
7. Quast, H.; Nahr, U. *Chem. Ber.* **1983**, *116*, 3427–3437.
8. Vandensavel, J.-M.; Smets, G.; Labbe, G., *J. Org. Chem.* **1973**, *38*, 675–678.
9. Tsuge, O.; Urano S.; Oe, K. *J. Org. Chem.* **1980**, *45*, 5130–5113.
10. Toselli, M.; Zanirato, P. *J. Chem. Soc. Perkin Trans. 1* **1992**, 1101–1104.
11. Salama, A. T.; Elmorsy, S. S.; Khalil, A.-G. M.; Ismail, M. A. *Chem. Lett.* **2011**, *40*, 1149–1151.
12. Deliomeroglu, M. K.; Ozcan, S.; Balci, M. *Arkivoc* **2010**, *2*, 148–160.
13. (a) Ozcan, S.; Sahin, E.; Balci, M. *Tetrahedron Lett.* **2007**, *48*, 2151–2154; (b) Ozcan, S.; Balci, M. *Tetrahedron* **2008**, *64*, 5531–5540.
14. (a) Goodridge, R. J.; Hambley, T. W.; Ridley, D. D. *Aust. J. Chem.* **1986***, 39*, 591 − 604. (b) Hall, H. K., Jr; Nogues, P.; Rhoades, J. W.; Sentman, R. C.; Detar, M. *J. Org. Chem.* **1982**, *47*, 1451 − 1455; (c) Ekmekci, Z.; Balci, M. *Eur. J. Org. Chem.* **2012**, 4988–4995.
15. Koza, G.; Ozcan, S.; Sahin, E.; Balci, M. *Tetrahedron* **2009**, *65,* 5973–5976.

16. Kita, Y.; Akai, S.; Ajimura, N.; Yoshigi, M.; Tsugoshi, T.; Yasuda, H.; Tamura, Y. *J. Org. Chem.* **1986**, *51,* 4150–4158.

17. Ozcan, S.; Dengiz, C.; Deliomeroglu, M. K.; Sahin, E.; Balci, M. *Tetrahedron Lett.* **2011,** *52,* 1495–1497.

18. Aluni, N. I.; Mark, P. K.; Allen, B. P. From PCT Int. Appl., 2006067444, 29 Jun **2006**.

19. (a) Lamblin, M.; Couture, A.; Deniau, E.; Grandclaudon, P. *Synthesis* **2006**, 1333–1338; (b) Kilikli, A. A.; Dengiz, C.; Ozcan, S.; Balci, M. *Synthesis* **2011**, 3697–3705.