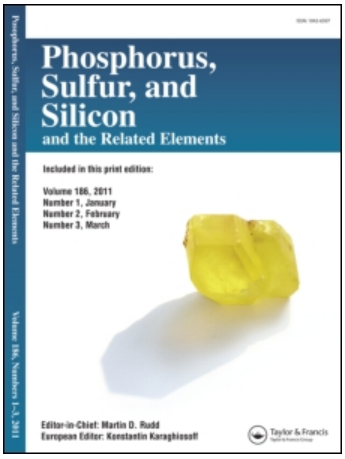

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Reaction of Dimethyl Acetylenedicarboxylate With 2-Mercaptoperimidine and 2-Mercaptobenzimidazole

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*A mixture of equimolar quantities of dimethyl acetylenedicarboxylate (**2**) with either 2-mercaptoperimidine (**1**) or 2-mercaptobenzimidazole (**5**) was heated in absolute benzene in the presence of triphenylphosphine as a catalyst under reflux conditions for 1 h (the reaction was monitored by TLC until the consumption of the starting materials). The solvent was concentrated under vacuum and the residue was subjected to chromatographic plates using toluene-ethylacetate (2:1) as an eluent. The products in each reaction were separated as two migrating zones. Each zone was removed from the plate and recrystallized from the appropriate solvent. The products of the first reaction are 10-methoxy-11-oxo-11*H*-8-thia-7,11*a*-diaza-benzo[*de*]anthracene-9-carboxylic acid methyl ester (**3**) and 8-thia-7,10*a*-diaza-cyclopenta[*a*]phenalene-9,10-dicarboxylic acid dimethyl ester (**4**), while the products of the second reaction are 3-methoxy-4-oxo-4*H*-1-thia-4*a*,9-diaza-fluorene-2-carboxylic acid methyl ester (**10**) and benzo[4,5]imidazo[2,1-*b*]thiazole-2,3-dicarboxylic acid dimethyl ester (**11**). The mechanisms of the observed reactions are suggested.*

Keywords 2-Mercaptobenzimidazole; 2-mercaptoperimidine; dimethyl acetylenedicarboxylate

INTRODUCTION

Both 2-mercaptoperimidine (**1**) and 2-mercaptobenzimidazole (**5**), as it might be readily obtained from 1,8-diaminonaphthalene and *o*-phenylenediamine, respectively, by treating with carbon disulfide in excellent yield,[1,2] have become important materials for the synthesis of a lot of heterocyclic compounds.[3–6] Dimethyl acetylenedicarboxylate (DMAD) has been used in the last few years for preparing several classes of organic compounds that might have high biological activity.[7–11] Where it reacts, for example, with heterocyclic thioamides,[12] N-substituted anilines,[13] 2,2-dithiodianilines[14] as well

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as salicylaldehyde[15] to yield thiazolin-4-one, quinoline-4-one, 1,4-benzothiazines, and benzopyranes (chromenes) derivatives, respectively. The reaction of the target DMAD with 2-mercaptoperimidine is not known yet. However, it was known by Grinblat and Postovskii[16] that on reacting DMAD with benzimidazole-2-thione, a thiazolo[3,2-*a*]benzimidazole derivative was obtained. This result was confirmed by Mckillop and colleagues.[17] While on treatment of 1*H*-benzimidazol-2-ylthio)acetonitrile with the same target in benzene, THF or DMF, [1,3]thiazolo[3,2-*a*]benzimidazole was obtained as the major product;[18] whereas on using aqueous ethanol, the major product was altered.[19]

RESULTS AND DISCUSSION

The present study aims to test the reactivity of DMAD towards both 2-mercaptoperimidine and 2-mercaptobenzimidazole. Equimolar amounts of dimethyl acetylenedicarboxylate and 2-mercaptoperimidine were dissolved in benzene in the presence of a catalytic amount of triphenylphosphine at r.t., and the mixture was heated under reflux conditions for 1 h. The solvent was evaporated under reduced pressure; the residue was subjected to plate chromatography using a mixture of toluene-ethyl acetate (2:1) as an eluent to get two zones in each reaction: the first reaction zones are 10-methoxy-11-oxo-11*H*-8-thia-7,11*a*-diaza-benzo[*de*]anthracene-9-carboxylic acid methyl ester (**3**) and 8-thia-7,10*a*-diaza-cyclopenta[*a*]phenalene-9,10-dicarboxylic acid dimethyl ester (**4**), as shown in Chart 1.

The structures of the obtained products were confirmed by their elemental analysis and spectral data; e.g., the IR spectrum of compound **3** shows strong absorption bands at $\nu = 1715$ and 1695 cm^{-1} that are characteristic for ester and imide carbonyl groups. The ^1H NMR spectrum shows, in addition to the aromatic protons, two singlets at $\delta = 3.92$, and 3.55 belongs to the two methoxy hydrogen protons. Moreover, the ^{13}C NMR spectrum shows, in addition to the aromatic carbons, two carbonyl groups at 167.40 and 164.64 ppm and two methoxy groups at 52.16 and 51.76 ppm. Furthermore, the mass spectrum confirms the structure of compound **3** where one can notice a molecular ion peak at 340, which is in accordance with the molecular weight of the compound as well

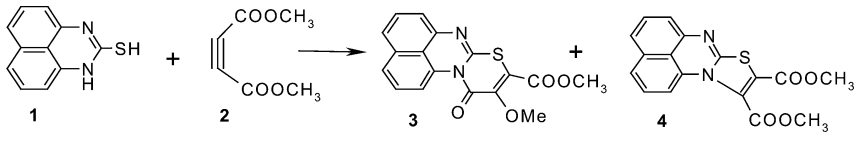

CHART 1 Reaction of 2-mercaptoperimidine (**1**) with dimethyl acetylene dicarboxylate (**2**).

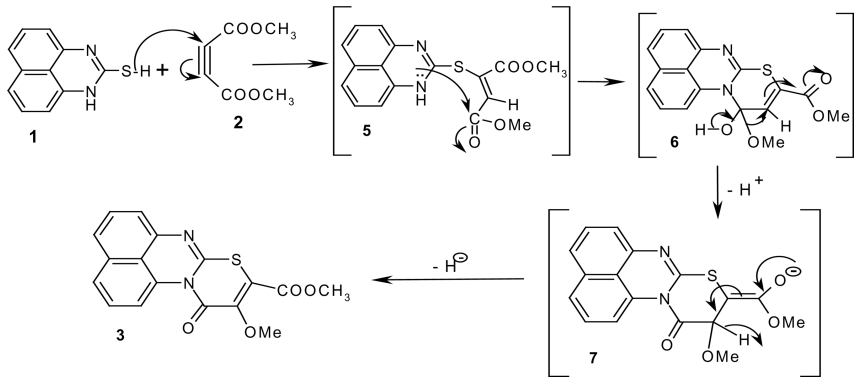

FIGURE 1 The suggeted mechanism for the formation of compound **3**.

as a base peak at 309, which referred to (M^+—OCH_3). The suggested mechanism for the formation of compound **3** is shown in Figure 1.

The lone pair of electrons of the S—H bond attacks on the acetylenic carbon atom to give the intermediate **5**. The unshared paired electron on the nitrogen atom attacks on the olefinic carbon to form the intermediate **9**, which losses on olecule of hydrogen to give the product **4**. Then the lone pair of the substituted nitrogen attacks to the ester's carbonyl group to give the intermediate **6**, which losses a proton through rearrangement to get the intermediate anion **7**, which changed to product **3** by losing a hydride ion.

The suggested mechanism for the formation of compound **4** is shown in Figure 2.

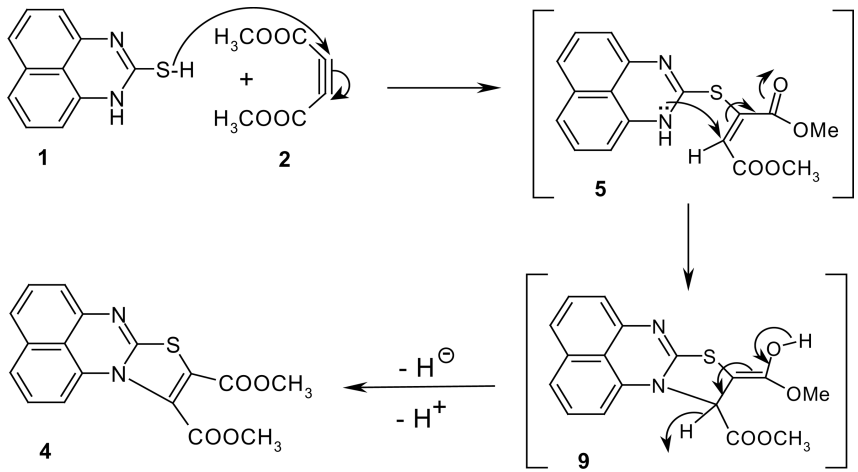

FIGURE 2 The suggested mechanism for the formation of compound **4**.

As shown in Figure 2, the (S—H) attacks the acetylenic bond (C≡C) to form intermediate **5**. Then the lone pair of the substituted nitrogen attacks the olefinic bond (C=C) to give the intermediate **9**, which losses a molecule of hydrogen to give product **4**. The analysis of compound **4** shows the following data: the two ester carbonyl groups appear in the IR spectrum at $\nu = 1738$ and 1712 cm^{-1}, while they appear in the ^{13}C NMR at $\delta = 165.96$ and 163.53 ppm. Furthermore, the ^{1}H NMR spectrum of this compound reveals, in addition to the aromatic protons, two singlets at $\delta = 4.09$ and 3.87, which are characteristic for two methyl ester's protons.

The mass spectrum gives the molecular ion peak at (m/z) = 340, which corresponds to the molecular weight of the compound, as well as a peak at m/z = 281, which is characteristic for (M^+—$COOCH_3$).

The second reaction zones that produced on reacting 2-mercapto-benzimidazole with dimethyl acetylenedicarboxylate are 3-methoxy-4-oxo-4*H*-1-thia-4*a*,9-diaza-fluorene-2-carboxylic acid methyl ester (**10**) and benzo[4,5]imidazo[2,1-*b*]thiazole-2,3-dicarboxylic acid dimethyl ester (**11**), as shown in Chart 2.

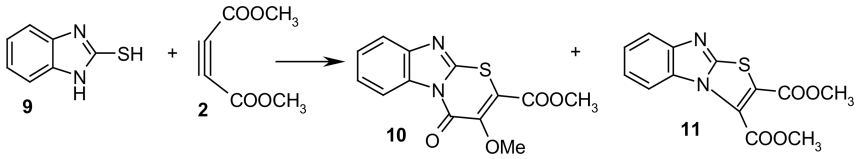

CHART 2 Reaction of 2-mercaptoperimidine (**9**) with dimethyl acetylene dicarboxylate (**2**).

The IR spectrum of compound **10** shows two absorption bands at 1731 and 1693 cm^{-1}, which are characteristic for the two carbonyl groups, while the two carbonyl groups of compound **11** appear at 1733 and 1718 cm^{-1}. The ^{13}C NMR spectrum of compound **10** shows, in addition to the aromatic carbon atoms, two carbonyl groups at 165.40, and 162.84 ppm. However, the two carbonyl groups of compound **11** exist in the ^{13}C NMR at 166.74 and 165.11 ppm. The mass spectrum reveals the molecular ion peaks of both compounds **10** and **11** at 290, but the fraction patterns of both compounds are different. Since compound **10** gives a base peak at 259, which corresponds to (M^+ —OCH_3), compound **11** gives a base peak at 231, which is compatible with (M^+ —$COOCH_3$).

EXPERIMENTAL

M.p.s have been determined in open glass capillaries on Gallen Kamp melting points apparatus and are uncorrected. The IR spectra were

recorded with Shimadzue 408 or a Bruker Vector 22 FT-IR instrument using potassium bromide pellets. A Bruker WM 400 instrument has been used to determine ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra; assigned of carbon resonances have been supported by DEPT 135/90 experiments. Mass spectra have been obtained with a Varian MAT 311 doubly focusing instrument using electron impact ionization (70 eV). Elemental analyses have been determined by the Microanalytical Center, Cairo University, Cairo, Egypt. Preparative layer chromatography; Glass plates 48 × 20 cm covered with slurry applied and air-dried layers of Merck Silica gel Pf_{254}. The detected zones were removed from plates and extracted with cold acetone.

STARTING MATERIAL

DMAD (Aldrich), 2-mercaptoperimidine, and 2-mercapto-benzimidazol were prepared according to the procedure.[20]

General Procedure for the Reaction of Dimethyl Acetylenedicarboxylate (2) with 2-Mercaptoperimidine (1) or 2-Mercaptobenzimidazole (9)

A mixture of 1 mmol of dimethyl acetylenedicarboxylate (**2**) and 1 mmol of either 2-mercaptoperimidine (**1**) or 2-mercaptobenzimidazole (**9**) in 20 mL of absolute benzene was heated under reflux conditions in the presence of a catalytic amount of triphenylphosphine for 1 h (the reaction was monitored by TLC until the consumption of the starting materials). The solvent was concentrated and the residue was subjected to chromatographic plates using toluene/ethylacetate (2:1) as an eluent. The products were separated as two migrating zones. Each zone was removed from the plate and recrystallized from the appropriate solvent.

*10-Methoxy-11-oxo-11*H*-8-thia-7,11*a*-diaza-benzo[*de*]anthracene-9-carboxylic Acid Methyl Ester (3)*

Red crystals (174 mg, 51%), m.p. = 167°C (CH_3CN), IR (KBr) ν = 1715 (CO), 1695 (CO), 1640 (C=N), 1589 (C=C); ^{1}H NMR ($CDCl_3$) δ = 7.21–7.11 (m, 3H, ArH), 7.05–6.85 (m, 3H, ArH), 3.92 (s, 3H, $-COOCH_3$), 3.55 (s, 3H, $-OCH_3$); ^{13}C NMR ($CDCl_3$) δ = 167.40, 164.64 (2 $\underline{C}O$), 161.79 ($\underline{C}$=N), 145.3, 137.0, 135.3, 133.91, 128.3, 126.5, 124.9, 123.04, 122.69, 119.03, 116.08, 109.87, 52.16, 51.76 (2 O$\underline{C}H_3$); MS (m/z) 340 (M^+), 309 ($M^+ - OCH_3$), 281, 253, 222, 178, 165, 154, 139, 111, 85, 77. Found: C, 59.70; H, 3.33; N, 8.02; S, 9.27. $C_{17}H_{12}N_2SO_4$ (340.36) calcd: C, 59.99; H, 3.55; N, 8.23; S, 9.42.

8-Thia-7,10a-diaza-cyclopenta[a]phenalene-9,10-dicarboxylic Acid Dimethyl Ester (4)

Pale-orange crystals (85 mg, 25%), m.p. = 183°C (CH_3CN), IR (KBr) ν = 1738 (ester CO), 1712 (CO), 1622 (C=N), 1585 (C=C); ^{1}H NMR ($CDCl_3$) δ = 7.34–7.20 (m, 1H, ArH), 7.16–7.00 (m, 4H, ArH), 6.66 (d, J = 6.9 Hz, 1H, ArH), 4.09 (s, 3H, –$COOCH_3$), 3.87 (s, 3H, –$COOCH_3$); ^{13}C NMR ($CDCl_3$) δ = 165.96 (CO), 163.53 (CO), 162.41 (C=N), 151.7, 148.2, 145.3, 137.5, 129.06, 127.2, 126.5, 123.7, 123.3, 119.1, 116.8, 114.9, 54.41, 52.90 (2 OCH_3); MS (m/z) 340, 281 (M^+ –$COOCH_3$), 222, 154, 140, 77. Found: C, 59.73; H, 3.39; N, 7.93; S, 9.19. $C_{17}H_{12}N_2SO_4$ (340.36) calcd.: C, 59.99; H, 3.55; N, 8.23; S, 9.42.

3-Methoxy-4-oxo-4H-1-thia-4a,9-diaza-fluorene-2-carboxylic Acid Methyl Ester (10)

Red crystals (116 mg, 40%), m.p. = 176°C (CH_3CN), IR (KBr) ν = 1731 (CO), 1693 (CO), 1642 (C=N), 1590 (C=C); ^{1}H NMR ($CDCl_3$) δ = 7.32–6.95 (m, 4H, ArH), 3.81 (s, 3H, –$COOCH_3$), 3.53 (s, 3H, –OCH_3); ^{13}C NMR ($CDCl_3$) δ = 165.40, 162.84 (2 CO), 141.79, 137.0, 136.83, 126.5, 124.9, 123.04, 122.69, 116.53, 116.08, 51.16, 50.76 (2 OCH_3); MS (m/z) 290 (M^+), 259 (M^+ –OCH_3), 231, 172, 91, 77. Found: C, 53.60; H, 3.35; N, 9.42; S, 10.87. $C_{13}H_{10}N_2SO_4$ (290.30) calcd.: C, 53.79; H, 3.47; N, 9.65; S, 11.05.

Benzo[4,5]imidazo[2,1-b]thiazole-2,3-dicarboxylic Acid Dimethyl Ester (11)

Yellow crystals (55 mg, 19%), m.p. = 163–165°C, (lit. 166–167°C,[18] 167–168°C[19]).

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