Synthesis of Naphthoquinone Derivatives. XIII. Reaction of 2,3-Dihydro-2-thioxo-1*H*-naphth[2,3-*d*]imidazole-4,9-dione with Dimethyl Acetylenedicarboxylate[1)]

Tateo NAKAMORI,* Toshiyuki SAITO, and Toshiyasu KASAI
Faculty of Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152
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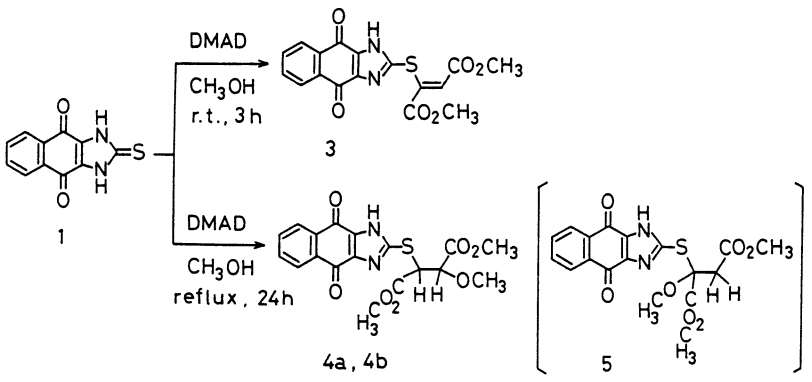
Tetracyclic compounds with a thiazolidinone or thiazinone ring fused to 1*H*-naphth[2,3-*d*]imidazole-4,9-dione were synthesized. Dimethyl 2-(4,9-dioxo-4,9-dihydronaphth[2,3-*d*]imidazol-2-ylthio)fumarate (**3**) was obtained by a reaction of 2,3-dihydro-2-thioxo-1*H*-naphth[2,3-*d*]imidazole-4,9-dione with dimethyl acetylenedicarboxylate in methanol. A ring-closure reaction of **3** in acetic anhydride was found to give selectively methyl (3,5,10-trioxo-2,3,5,10-tetrahydronaphth[2′,3′:4,5]imidazo[2,1-*b*]thiazol-2-ylidene)acetate, while, the cyclization of **3** in polyphosphoric acid afforded methyl 4,6,11-trioxo-6,11-dihydro-4*H*-naphth[2′,3′:4,5]imidazo[2,1-*b*]-thiazine-2-carboxylate.

1,4-Naphthoquinone derivatives fused with the azole ring have attracted much attention because of their physiological and coloring properties. However, a few reports[2)] have appeared in the literature which have described the synthesis of tetracyclic azole compounds. In our previous papers, we reported on the syntheses of imidazo[2,1-*b*]naphtho[2,3-*d*]thiazole-5,10-diones[3a)] and naphth[2′,3′:4,5]imidazo[2,1-*b*]thiazole-5,10-diones,[3b,c)] showing physiological activities. We then developed a convenient method for the synthesis of 2,3-dihydro-2-thioxo-1*H*-naphth[2,3-*d*]imidazole-4,9-dione (**1**). We were also interested in the syntheses of tetracyclic azole compounds, which may be easily available from compound **1**. This paper describes the preparation of tetracyclic azole compounds, fused thiazolidione or thiazinone ring from dimethyl 2-(4,9-dioxo-4,9-dihydronaphth[2,3-*d*]imidazol-2-ylthio)-fumarate (**3**), which was obtained by a Michael-type reaction of **1** with dimethyl acetylenedicarboxylate (DMAD). Furthermore, the effects of the quinone carbonyl groups on the cyclization reactions will be discussed.

Results and Discussion

A few reports[4)] concerning reactions of 2*H*-benzimidazole-2-thione (**2**) with DMAD have already appeared. A recent report by Wade[4a)] indicated that a reaction in methanol yields methyl 4-oxo-4*H*-[1,3]-thiazino[3,2-*a*]benzimidazole-2-carboxlate in one step. We first investigated the reaction of the thione **1** with DMAD by the method of Wade. When a solution of **1** with DMAD in methanol was stirred at room temperature for 3 h, the adduct **3** was isolated in 74% yield. A structural assignment for the product **3**, depending on the sulfur atom participates in the addition reaction, was accomplished through its ^{1}H NMR and IR spectra. The (*Z*)-geometry of **3**, which results from a trans addition, is assumed on the basis of the results of Hendrickson[5a)] and Truce[5b)] (Scheme 1). On the other hand, a reaction of **1** with DMAD at reflux temperature for 24 h gave yellow crystals **4a** (mp 171.0—172.0 °C, 11%) and **4b** (mp 131.0—132.0 °C, 15%). Also, compounds **4a** and **4b** were obtained from adduct **3** under the same conditions. The structures of diastereoisomers **4a** and **4b** formed by the addition of methanol to **3** were established on the basis of IR, ^{1}H NMR, and elemental analysis data. The structure of diastereoisomer **4b** was supported, rather than structure **5**, since there was little variation in the yield between **4a** and **4b**, and the proton coupling constant of **4a** and **4b** showed 3.5 and 5 Hz, respectively.

The reaction was carried out in the presence of sodium methoxide as a base in methanol, in order to



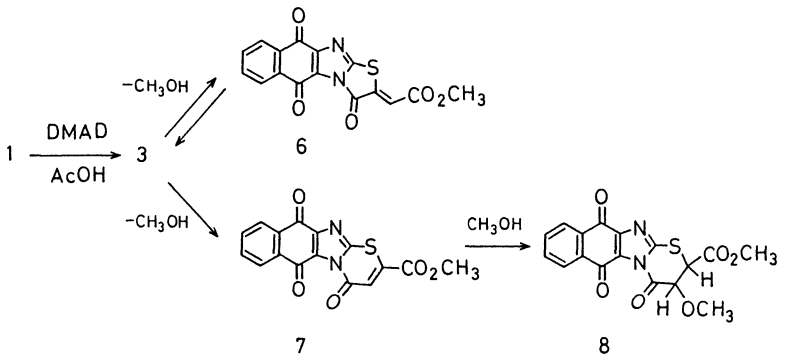
Scheme 1.

obtain cyclized compounds, i.e., methyl (3,5,10-trioxo-2,3,5,10-tetrahydronaphth[2′,3′ : 4,5]imidazo[2,1-*b*]thiazol-2-ylidene)acetate (**6**), methyl 4,6,11-trioxo-6,11-dihydro-4*H*-naphth[2′,3′ : 4,5]imidazo[2,1-*b*]thiazine-2-carboxylate (**7**). Compound **1** gave adduct **3** at room temperature for 30 min, but for prolonged reaction times compound **6** or **7** was not isolated but compound **1** formed by the methanolysis of **3** was recovered. These results could be explained in terms of the nucleophilicity of nitrogen in the imidazole ring being diminished by means of the electron-withdrawing character of the quinonoid moiety.

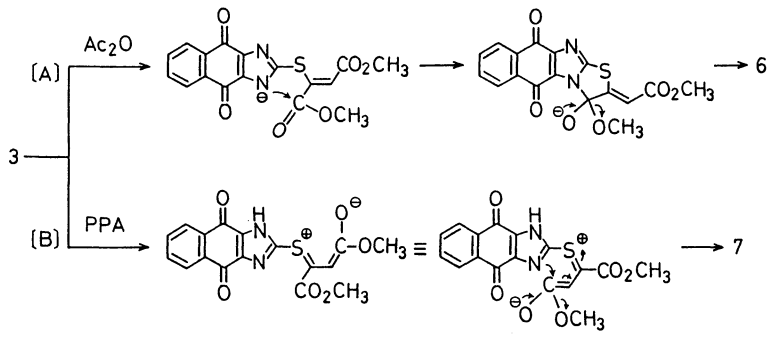
However, a mixture of **1** and DMAD in acetic acid was refluxed for 3 h to give the two isomers (**6** and **7**) in 22% yield, which could not be separated by column chromatography. The ^{1}H NMR analysis showed that **6** and **7** were produced in the ratio of 7 : 4. (Pure **6** and **7** were prepared from the adduct **3** individually as mentioned later.) In addition, when the reaction was carried out for 24 h, compound **8** (mp 209.0—210.0 °C) was unexpectedly obtained in 31% yield without the formation of **6** and **7**. The formation of **8** may involve the addition of methanol eliminated to the thiazinone ring of **7**. The position of the methoxyl group in compound **8** was determined by the ^{1}H NMR spectrum, which shows *vicinal* H_2 and H_3 protons at δ 5.98 and 5.07 ($J_{2,3}$=2 Hz), respectively. Furthermore, the H_7 proton of compound **8** appears at a lower field, compared with the other protons in the aromatic ring.[6] This downfield shift may be explained on the basis that the 4-oxo function is held in a rigid position, coplanar with and oriented toward the aromatic ring, thus exerting a deshielding effect on the H_7 proton. Secondly, the cyclization of adduct **3** using condensing agents[7,8] was investigated.

The solution of **3** in acetic anhydride was heated at 100 °C for 20 min to afford compound **6** in 42% yield. A prolonged reaction time did not show any increase in the yield of compound **6** nor in the formation of compound **7**. The formation of **6** might involve an attack of the nitrogen situated closely to the ester moiety (Scheme 3, route A). Under these conditions, using acetic anhydride acetylation on the nitrogen atom is postulated to be an initial reaction. It seems, however, that the acetylation does not occur because ethyl 3-(4,9-dioxo-4,9-dihydronaphth[2,3-*d*]imidazol-2-ylthio)acrylate (**9**) reacted unchanged in acetic anhydride, as will be mentioned later. On the other hand, the reaction of **3** in polyphosphoric acid (PPA) at 140—150 °C for 30 min gave compound **7** in 66% yield as the sole product. One possible mechanistic pathway to **7** is shown in route B of Scheme 3. Of particular interest is the selective formation into **6** and **7**. The structures of **6** and **7** were determined by the ^{1}H NMR spectra. In addition, to make this analysis more complete, we wanted to prepare a compound with a thiazinone ring like that of the structure of **7** by employing the alternative procedure shown in Scheme 4.

A suspension of **1** and ethyl propiolate in ethanol was refluxed for 5 h to afford a yellow compound **9a** (mp 260.5—262.0 °C) and an orange compound **9b** (mp 233.0—234.0 °C) in 29 and 48% yield, respectively. The



Scheme 2.



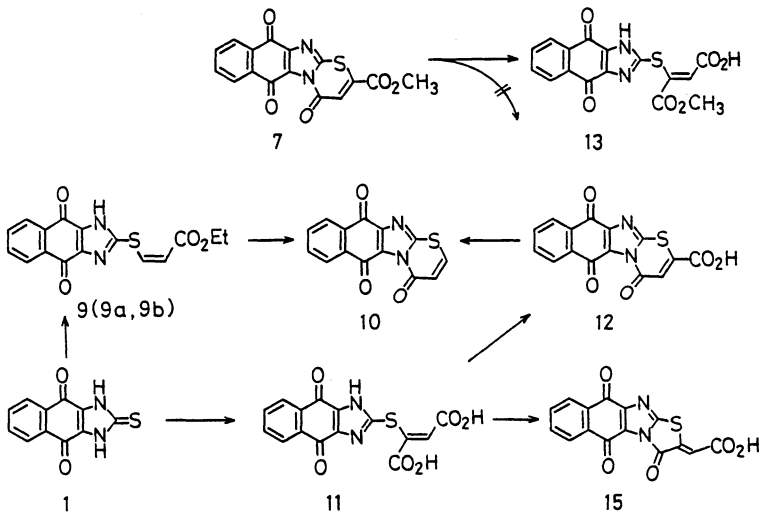
Scheme 3.

^{1}H NMR spectra of **9a** (*Z* form /trans addition product) and **9b** (*E* form /cis addition product) showed two doublets for the olefinic protons at δ 6.31 and 8.23 (J=10 Hz) and at 6.46 and 8.32 (J=16 Hz), respectively. The coupling constants were consistent with these geometorical assignments. The formation of the two isomers is of interest since the reaction of **1** with DMAD gave a single isomer (as mentioned above). No isomerization of **9a** to **9b** was observed under reflux in ethanol.

A cyclization of **9** is expected to produce compound **10** with a fused thiazinone ring. A suspension of **9a** or **9b** in PPA was heated to afford **10**: mp 265 °C (decomp); no reaction occurred in acetic anhydride. This result is in accord with the above-mentioned expectation. The synthesis of compound **10** via **12** from **7**, obtained by a reaction of **1** with DMAD, was tried. However, the hydrolysis of **7** with sodium hydroxide did not give compound **12** but, rather, compound **13** via a cleavage of the thiazinone ring; also, a reaction with hydrochloric acid or sulfuric acid did not give any isolable compound. The hydrolysis of **6**, as well as **7**, gave the monomethyl ester of fumaric acid (**14**). It is thus thought that the amide bond in the thiazolidinone or thiazinone ring was easily cleavaged since the quinone-carbonyl groups result in a decrease in the nucleophilicity of the nitrogen atom. Attempts to obtain compound **12** by the hydrolysis of **7** were unsucessful.

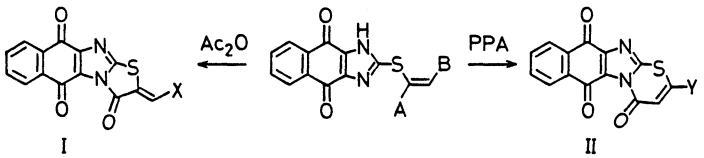
Compound **12** was finally obtained in PPA from adduct **11**, prepared by a reaction of **1** with acetylenedicarboxylic acid. A decarboxylation of **12** by thermolysis in biphenyl-diphenyl ether (1:3) at 250 °C afforded compound **10**, while the cyclization of **11** in acetic anhydride gave compound **15**. Furthermore, the $\nu_{C=O}$ of **12** and **15** were similar to those of **7** and **6**, respectively. These results suggest that compound **7** or **6** has a fused thiazinone or thiazolidinone ring, respectively.

The cyclization of the other related adducts in PPA and acetic anhydride are summarized in Table 1. It is of interest that the cyclization of **13** in acetic anhydride and of **14** in PPA gave the methyl esters, **6** and **7**, respectively, which might be formed via a further reac-



Scheme 4.

Table 1. Cyclization of the Adducts in Acetic anhydride or Polyphosphoric Acid (PPA)



Substrate			Product			
			[I]		[II]	
Compd No.	A	B	Compd No.	X	Compd No.	Y
3	COOMe	COOMe	**6**	COOMe	**7**	COOMe
13	COOMe	COOH	**6**	COOMe	**7**	COOMe
14	COOH	COOMe	**6**	COOMe	**7**	COOMe
11	COOH	COOH	**15**	COOH	**12**	COOH
9	H	COOEt	No reaction		**10**	H

tion of **12** with methanol eliminated during the reaction.

In summary, tetracyclic azole compounds with a fused thiazolidinone or thiazinone ring were obtained from adduct **3**, prepared by the reaction of **1** with DMAD. It was found that the cyclization of **3** gave compound **6** or **7** by the use of acetic anhydride or PPA as an effective condensing agent, respectively.

Physiological evaluations of the synthesized compounds are currently under way and the results will be reported elesewhere.

Experimental

Measurements. The melting points were determined with a Yamato MP-1 apparatus and are uncorrected. IR spectra were taken on a JASCO IRA-1 spectrophotometer using KBr pressed discs. ^{1}H NMR spectra were recorded on a JEOL PS-100 (100MHz) spectrometer. Chemical shifts are given in ppm relative to tetramethylsilane as an internal standard. Mass specra were taken on a Hitachi RMU-7M mass spectrometer at an ion-source temperature of 200 °C and an ionizing potential of 75 eV.

Dimethyl 2-(4,9-Dioxo-4,9-dihydronaphth[2,3-*d*]imidazol-2-ylthio)fumarate (3). DMAD (0.65 g, 4.57 mmol) in 5 cm^3 of methanol was added dropwise with stirring to a suspension of the thione **1** (1.0 g, 4.35 mmol) in 15 cm^3 of methanol. After being stirred for 3 h at room temperature, the solid was collected by filtration, washed with ether, and dried to give 1.20 g (74%) of **3** (mp 204.0—206.0 °C). Recrystallization from ethyl acetate-hexane gave 0.74 g (46%) of pure **3** as yellow plates: mp 207.0—209.0 °C; IR 3215 (NH), 1715 and 1675 (C=O), 1600, 1418, 1337, 1275, 1220, 1065, and 980 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ=3.57 (3H, s), 3.78 (3H, s), 6.86 (1H, s), 7.78—7.96 (2H, m), 7.98—8.18 (2H, m); MS *m/z* (rel intensity) 372 (M$^+$; 3), 342 (13), 341 (30), 340 (35), 283 (8), 282 (12), 281 (55), 260 (12), 259 (55), 258 (100), 255 (13), and 254 (50). Found: C, 54.91; H, 3.11; N, 7.58; S, 8.67%. Calcd for $C_{17}H_{12}N_2O_6S$: C, 54.84; H, 3.25; N, 7.52; S, 8.61%.

Methanol Addition to 3. A suspension of **3** (0.50 g, 1.34 mmol) in 20 cm^3 of methanol was heated at refluxing temperature for 24 h. After the mixture was allowed to stand overnight, the solid was collected by filtration, washed with ether, and dried to give 0.13 g of crude **4b** (mp 104.0—106.0 °C). Recrystallization from benzene gave 0.08 g (15%) of pure **4b** as a yellow powder: mp 131.0—132.0 °C; IR 3190 (NH), 2940 (CH), 1725 and 1670 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=3.52 (3H, s), 3.82 (3H, s), 3.85 (3H, s), 4.39 (1H, d, J=5 Hz), 4.85 (1H, d, J=5 Hz), 7.63—7.81 (2H, m), 8.05—8.30 (2H, m). Found: C, 53.60; H, 4.34; N, 6.41; S, 7.48%. Calcd for $C_{18}H_{16}N_2O_7S$: C, 53.47; H, 3.96; N, 6.93; S, 7.92%. To the mother liquor was added 100 cm^3 of water and was extracted with chloroform. The solution was evaporated under reduced pressure, giving 0.06 g (11%) of a yellow powder (mp 171.0—172.0 °C). Recrystallization from benzene-hexane gave 0.05 g of pure **4a**: mp 172.0—173.0 °C; IR 3300 (NH), 2920 (CH), 1740 and 1665 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=3.58 (3H, s), 3.80 (6H, s), 4.61 (1H, d, J=3.5 Hz), 5.02 (1H, d, J=3.5 Hz), 7.56—7.73 (2H, m), 8.00—8.18 (2H, m). Found: C, 53.49; H, 3.81; N, 6.93; S, 7.78%. Calcd for $C_{18}H_{16}N_2O_7S$: C, 53.47; H, 3.96; N, 6.93; S, 7.92%.

Methyl (3,5,10-Trioxo-2,3,5,10-tetrahydronaphth[2′,3′:4,5]-imidazo[2,1-*b*]thiazol-2-ylidene)acetate (6). A suspension of **3** (1.00 g, 2.69 mmol) in 20 cm^3 of acetic anhydride was heated at 100 °C for 20 min. After the mixture was allowed to come to room temperature, the solid was filtered off, washed with ether, and dried to give 0.38 g (42%) of **6** as yellowish green crystals. Recrystallization from chlorobenzene gave 0.23 g (25%) of pure **6**: mp 248.0 °C (decomp); IR 3050 (CH), 1770, 1725, 1680, and 1665 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=3.93 (3H, s), 7.32 (1H, s), 7.70—7.88 (2H, m), 8.12—8.32 (2H, m); MS *m/z* (rel intensity) 342 (M$^+$+2; 10), 341 (M$^+$+1; 9), 340 (M$^+$; 100), 312 (10), 309 (10), 283 (13), 282 (12), 281 (37), 258 (13), 255 (21), 254 (67). Found: C, 56.40; H, 2.34; N, 7.90; S, 9.24%. Calcd for $C_{16}H_8N_2O_5S$: C, 56.47; H, 2.35; N, 8.24; S, 9.42%.

Methyl 4,6,11-Trioxo-6,11-dihydro-4*H*-naphth[2′,3′:4,5]-imidazo[2,1-*b*]thiazine-2-carboxylate (7). A suspension of **3** (1.35 g, 3.63 mmol) in ca. 60 g of PPA was heated at 140—150 °C for 30 min. The reaction mixture was allowed to cool and then suspended in 300 cm^3 of water. The solid was collected by filtration, washed with acetone, and dried to yield 0.81 g (66%) of crude **7**: mp 245.0 °C (decomp). Recrystallization from 1-butanol gave 0.57 g (46%) of pure **7** as yellow needles: mp 255.0 °C (decomp); IR 3060 (CH), 1727, and 1680 cm^{-1} (C=O): ^{1}H NMR ($CDCl_3$) δ=4.06 (3H, s), 7.56 (1H, s), 7.68—7.84 (2H, m), 8.14—8.30 (2H, m); MS *m/z* (rel intensity) 342 (M$^+$+2; 30), 341 (M$^+$+1; 21), 340 (M$^+$; 100), 312 (10), 284 (16), 282 (10), 281 (20), 255 (12), 254 (24). Found: C, 56.26; H, 2.21; N, 8.21; S, 9.32%. Cacld for $C_{16}H_8N_2O_5S$: C, 56.47; H, 2.35; N, 8.24; S, 9.42%.

Methyl 3-Methoxy-4,6,11-trioxo-3,4,6,11-tetrahydro-2*H*-naphth[2′,3′:4,5]imidazo[2,1-*b*]thiazine-2-carboxylate (8). A suspension of DMAD (0.13 g, 0.91 mmol) in 3 cm^3 of acetic acid was added with stirring to a suspension of **1** (0.20 g, 0.87 mmol) in **2** cm^3 of acetic acid. After refluxing for 24 h, an insoluble solid was filtered off and the filtrate was left standing overnight in an ice box. The solid was collected by filtration, dried to give 0.18 g of yellow crystals and chromatographed on a Wakogel C-200 column using chloroform as an eluant. The evaporation residue from the second fraction gave 0.10 g (31%) of **8** as yellow needles: mp 209.0—211.0 °C; IR 2965 (CH), 1740, 1683, and 1660 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=3.86 (6H, s), 5.07 (1H, d, J=2 Hz), 5.98 (1H, d, J=2 Hz), 7.64—7.80 (2H, m), 8.04—8.17 (1H, m), 8.19—8.32 (1H, m). Found: C, 54.73; H, 3.10; N, 7.30; S, 8.13%. Calcd for $C_{17}H_{12}N_2O_6S$: C, 54.83; H, 3.25; N, 7.52; S, 8.61%.

Ethyl 3-(4,9-Dioxo-2-naphth[2,3-*d*]imidazolylthio)acrylate (9). Ethyl propiolate (0.24 g, 2.39 mmol) in 5 cm^3 of ethanol was added with stirring to a suspension of **1** (0.50 g, 2.17 mmol) in 10 cm^3 of ethanol and refluxed for 5 h. The solid was filtered off, washed with ether and dried to yield 0.68 g (95%) of **9**. Recrystallization from acetone gave 0.21 g (29%) of **9a** (*Z* form: mp 260.5—262.0 °C) as yellow needles. Crude **9a** was recrystallized from ethyl acetate-hexane to give pure **9a**: mp 263.0—264.0 °C; IR 3180 (NH), 3090, 3060, 2985 (CH), 1700, and 1680 cm^{-1} (C=O); ^{1}H NMR (DMSO-d_6) δ=1.24 (3H, t, J=7 Hz), 4.18 (2H, q, J=7 Hz), 6.31 (1H, d, J=10 Hz), 7.76—7.92 (2H, m), 8.01—8.15 (2H, m), 8.23 (1H, d, J=10 Hz); MS *m/z* (rel intensity) 329 (M$^+$+1, 1), 328 (M$^+$, 1), 285 (1), 284 (2), 283 (7), 282 (2), 267 (1), 258 (2), 257 (7), 256 (17), 255 (100), 254 (2), 231 (5), 230 (17). Found: C, 58.47; H, 3.55; N, 8.44; S, 9.82%. Calcd for $C_{16}H_{12}N_2O_4S$: C, 58.54; H, 3.66; N, 8.54; S, 9.77%. The filtrate of acetone recrystallization was evaporated and the residue was recrystallized from

chloroform and ethanol to give 0.34 g (48%) of **9b** (*E* form: mp 233.0—234.0 °C) as orange needles: IR 3125 (NH), 3085, 3035, 2985 (CH), 1695, 1685, and 1662 cm^{-1} (C=O); ^1H NMR (DMSO-d_6) δ=1.26 (3H, t, J=7 Hz), 4.24 (2H, q, J=7 Hz), 6.46 (1H, d, J=16 Hz), 7.84—8.05 (2H, m), 8.08—8.30 (2H, m), 8.32 (1H, d, J=16 Hz). Found: C, 59.32; H, 3.58; N, 8.58; S, 9.87%. Calcd for $C_{16}H_{12}N_2O_4S$: C, 58.54; H, 3.66; N, 8.54; S, 9.77%.

***4H*-Naphth[2′,3′:4,5]imidazo[2,1-*b*]thiazine-4,6,11-trione (10).** This compound as yellow needles: mp 265.0 °C (decomp) was obtained in 66% yield from **9a** using conditions similar to those described for **7**. IR 3030, 3000 (CH), 1715, and 1663 cm^{-1} (C=O); ^1H NMR (DMSO-d_6) δ=6.93 (1H, d, J=10 Hz), 7.81—7.95 (2H, m), 8.04—8.16 (2H, m), 8.35 (1H, d, J=10 Hz); MS m/z (rel intensity) 284 (M^++2, 12), 283 (M^++1, 21), 282 (M^+, 100), 255 (6), 254 (26), 238 (12), 230 (6). Found: C, 59.99; H, 1.98; N, 9.94; S, 11.34%. Calcd for $C_{14}H_6N_2O_3S$: C, 59.57; H, 2.13; N, 9.93; S, 11.35%.

2-(4,9-Dioxo-4,9-dihydronaphth[2,3-*d*]imidazol-2-ylthio)-fumaric Acid (11). Acetylenedicarboxylic acid (0.28 g, 2.45 mmol) in 5 cm^3 of acetonitrile was added to a suspension of **1** (0.50 g, 2.17 mmol) in 5 cm^3 of acetonitrile. After being stirred for 10 h at room temperature, the solid was collected by filtration, washed with ether, and dried to give 0.66 g (88%) of **11** as yellow crystals: mp 218.0 °C (decomp): IR 3300 (NH), 3050 (CH), and 1710—1670 cm^{-1} (C=O); ^1H NMR (DMSO-d_6) δ=6.90 (1H, s), 7.83—8.07 (2H, m), 8.08—8.27 (2H, m). Found: C, 52.56; H, 2.60; N, 7.61; S, 9.03%. Calcd for $C_{15}H_8N_2O_6S$: C, 52.33; H, 2.33; N, 8.14; S, 9.30%.

4,6,11-Trioxo-6,11-dihydro-4*H*-naphth[2′,3′:4,5]imidazo-[2,1-*b*]thiazine-2-carboxylic Acid (12). This compound as yellow plates: mp 252.0 °C (decomp) was obtained in 42% yield from **11** using conditions similar to those described for **7**. IR 3400 (OH), 1730 and 1673 cm^{-1} (C=O); MS m/z (rel intensity) 326 (M^+, 2), 285 (3), 284 (17), 283 (24), 282 (100), 256 (3), 255 (6), 254 (25), 239 (3), 238 (12), 232 (2), 231 (6), 230 (26). Found: C, 55.76; H, 1.61; N, 8.67; S, 10.12%. Calcd for $C_{15}H_6N_2O_5S$: C, 55.22; H, 1.84; N, 8.59; S, 9.82%.

(3,5,10-Trioxo-2,3,5,10-tetrahydronaphth[2′,3′:4,5]imidazo-[2,1-*b*]thiazol-2-ylidene)acetic Acid (15). A suspension of **11** (0.50 g, 1.45 mmol) in 5 cm^3 of acetic anhydride was heated at 100—110 °C for 10 min. The solid was collected by filtration, washed with ether, and dried to yield 0.36 g (76%) of **15** as yellow crystals: mp 255.0 °C (decomp): IR 3250—2800 (broad, OH), 1855, 1840, 1773, and 1670 cm^{-1} (C=O); MS m/z (rel intensity) 326 (M^+, 19), 284 (4), 283 (9), 282 (23), 256 (4), 255 (14), 254 (55), 238 (4), 232 (7), 231 (23), 230 (100).

Decarboxylation of 12. A suspension of **12** (0.10 g, 0.31 mmol) in 8.0 g of biphenyl-diphenyl ether (1 : 3) was heated at 250 °C for 10 min. The solid was collected by filtration, washed with hexane and ether, and dried to yield 0.07 g (80%) of **10**. This compound was identical as **10** on the basis of IR spectrum and mixed melting point.

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