Synthesis of 1-Azacycl[3.2.2]azine and 1-Azabenzo[*h*]cycl[3.2.2]azine

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1-Azacycl[3.2.2]azines were synthesized from 2-methylthioimidazo[1,2-*a*]pyridines, **2a** and **2b**, by using [2 + 8] cycloaddition reaction with dimethyl acetylenedicarboxylate as the key step. Synthesis of 1-azabenzo-[*h*]cycl[3.2.2]azine was also described.

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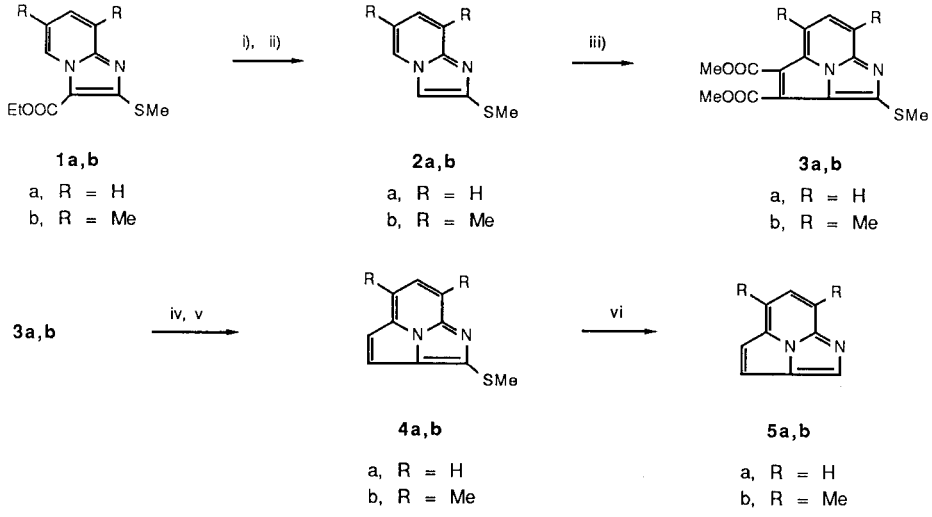
1-Azacycl[3.2.2]azine is an aromatic compound involving delocalized 10 π-electrons similarly to cycl[3.2.2]azines [1-3]. Synthesis of cycl[3.2.2]azines by the [2 + 8] cycloaddition reaction of indolizines with various acetylenic compounds is useful as a particularly convenient and general method, since it has been disclosed that dimethyl acetylenedicarboxylate (DMAD) reacts with indolizines in the presence of dehydrogenating reagent to give cycl-[3.2.2]azine derivatives [1-4]. Some azacycl[3.2.2]azine derivatives are also prepared by [2 + 8] cycloaddition reaction [5-8]. However, the reaction of DMAD with aza-indolizines, which are not substituted on the five-membered ring, does not give the desired cyclazine derivatives. This point is a drawback of the above reaction. Therefore, in an extension of the cycloaddition reaction as shown above, appropriate 2-substituted imidazo-[1,2-*a*]pyridine derivatives whose substituent may be removable after the cycloaddition reaction should be chosen. Thus 2-methylthioimidazo[1,2-*a*]pyridine is the most suitable starting material for the synthesis of 1-azacycl[3.2.2]azines. We have recently reported the facile synthesis of ethyl 2-methylthioimidazo[1,2-*a*]pyridine derivatives in good yields [9]. In this paper, we now wish to report the synthesis of 1-azacycl[3.2.2]azine derivatives using 2-methylthioimidazo[1,2-*a*]pyridines as key intermediates and also describe benzannelated 1-azacycl-[3.2.2]azine, 1-azabenzo[*h*]cycl[3.2.2]azine (**13**) by the similar methodology.

Deesterification of **1a** using sodium hydroxide in methanol followed by treatment with polyphosphoric acid (PPA) gave the corresponding 2-methylthioimidazo[1,2-*a*]-pyridine in 92% yield. The reaction of **2a** with DMAD in boiling toluene in the presence of palladium on charcoal gave a cyclized product, dimethyl 2-methylthio-1-azacycl-

Chart 1



i) 10% NaOH, HCl; ii) PPA; iii) DMAD, Pd-C in toluene;
iv) 10% NaOH, HCl; v) CuCrO4 in diphenylether; vi) Raney–Ni

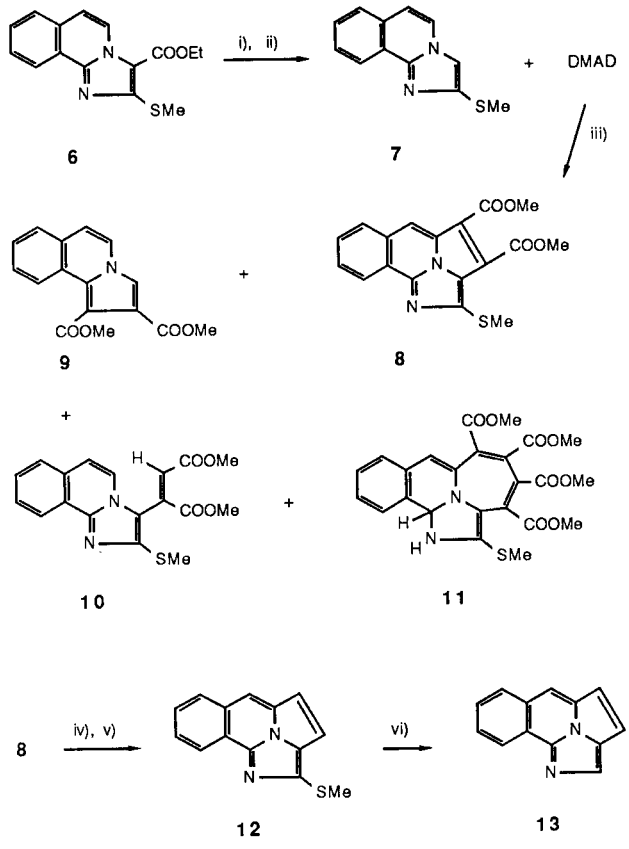
[3.2.2]azine-3,4-dicarboxylate (**3a**), in 36% yield. Hydrolysis of **3a** using sodium hydroxide in methanol followed by acidification with 10% hydrogen chloride gave the corresponding diacid. Decarboxylation of the diacid was conducted by copper chromate in boiling diphenyl ether (*ca.* 200°) to afford 2-methylthio-1-azacycl-[3.2.2]azine (**4a**) in 42% yield. The desulfurization of **4a** with Raney-nickel in ethanol solution occurred smoothly to give a desired parent 1-azacycl[3.2.2]azine (**5a**) in 34% yield. 5,6-Dimethyl-1-azacycl[3.2.2]azine (**5b**) was also synthesized in good yield from 2-methylthio-6,8-dimethylimidazo[1,2-*a*]pyridine (**2b**) in a similar manner to that described for **5a**. This compound was a very stable yellow needles, mp 106°.

Next, we attempted to synthesize 1-azabenzo[*h*]cycl-[3.2.2]azine [10]. In recent years considerable effort has been directed to elucidate the effect of benzo-fusions on annulene systems showing aromaticity [11]. Of interest and of central importance has been the question whether the delocalization in the cyclazine and azacyclazine is reduced by benzannelation on the macrocyclic ring or lost at all. We have recently described the synthesis of mono- and dibenzo-annelated cycl[3.2.2]azine derivatives which are very stable and typical delocalized 14π or 18π electron aromatic compounds [12-14].

Hydrolysis of **6** with sodium hydroxide in methanol to the corresponding carboxylic acid and subsequent decarboxylation of the acid by heating in polyphosphoric acid gave the desired compound **7**. A solution of **7** and DMAD in toluene was refluxed for 30 hours using a 5% palladium on charcoal to give the expected dimethyl 2-methylthio-1-azabenzo[*h*]cycl[3.2.2]azine-3,4-dicarboxylate (**8**), though in 6% yield, together with dimethyl pyrrolo[2,1-*a*]isoquinoline-2,3-dicarboxylate (**9**) (33%), methyl (2-methylthioimidazo[2,1-*a*]isoquinolinl-3-yl)-α-methoxycarbonylacrylate (**10**), and tetramethyl 1,11b-methylthio-1-azabenzo[*g*]cycl-[4.3.2]azine-3,4,5,6-tetracarboxylate (**11**) (2%). Hydrolysis of **8** with 10% sodium hydroxide gave the corresponding diacid almost quantitatively. Decarboxylation of diacid occurred smoothly on heating with copper chromate in diphenyl ether to produce 2-methylthio-1-azabenzo[*h*]cycl-[3.2.2]azine (**12**) in 34% yield. Finally, desulfurization of **12** was easily attained by a catalysis of Raney-nickel to afford the desired parent compound, 1-azabenzo[*h*]cycl-[3.2.2]azine (**13**) in 15% yield.

Both the 1-azabenzo[*h*]cycl[3.2.2]azines, **12** and **13** are yellow crystals and soluble in most of organic solvents giving pale yellow solutions. They are stable to heat, light, and acids. The aromatic proton chemical shifts (7.40-9.04 ppm) of **13** in the ^{1}H nmr spectrum are similar to those of benzo[*g*]cycl[3.2.2]azine (7.28-8.95 ppm) and of 1-azacycl-[3.2.2]azine (**5a**) (7.46-8.58 ppm). The vicinal coupling constant between C3-H and C4-H ($J_{3,4}$ = 5.0 Hz) is slighly

Chart 2



i) 10% NAOH, HCl; ii) PPA; iii) Pd-C in toluene;
iv) 10% NaOH, HCl NaOH, HCl; v) $CuCrO_4$ in diphenylether; vi) Raney–Ni

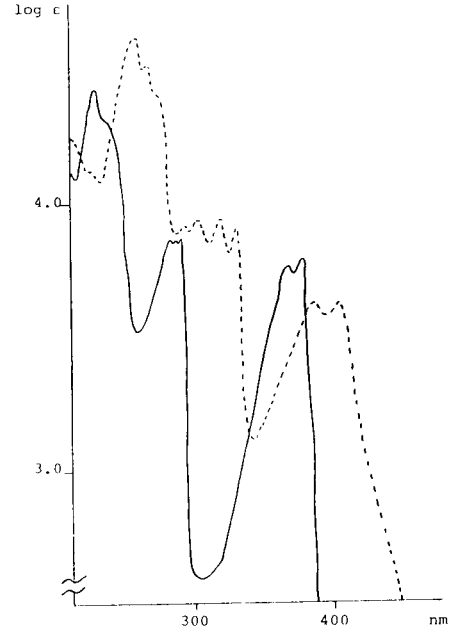


Figure 1. Uv spectra of **5a** and **13** in ethanol; **5a**: ——— ; **13**: ·····.

larger than the corresponding value in **5a** and benzo[*g*]-cycl[3.2.2]azine (4.8 and 4.9 Hz). The methyl protons (2.94 ppm) of methylthio group of **12** are strongly deshielded relative to those (2.03-2.33 ppm) of the nonaromatic model compounds such as ketene dithioacetals. The uv spectra of **5a** and **13** are shown in Figure 1. The major bands of **13** absorbed at 257, 317, 385, and 404 are bathochromically shifted from the parent compound **5a** absorbed at 226, 291, 368, and 378, respectively, consistently with longer conjugated aromatic system. The above results apparently show that 1-azabenzo[*h*]cycl[3.2.2]azine derivatives, **12**, **13**, are typical aromatic compounds.

2-Methylthioimidazo[1,2-*a*]pyridines and 2-methylthioimidazo[2,1-*a*]isoquinolines are very useful synthetic intermediates for the preparation of 1-azacycl[3.2.2]azine derivatives. Further studies are actively in progress including the synthesis of the other azacyclazine derivatives.

EXPERIMENTAL

All melting points were determined in a capillary tube and uncorrected. Infrared (ir) spectra were recorded in potassium bromide pellets on JASCO IRA-2 spectrometer and ultraviolet (uv) absorption spectra were determined in 95% ethanol on a Hitachi EP-S2 spectrometer. Nuclear magnetic resonance (nmr) spectra were obtained on JNM-PS-100 (100 MHz) and JNM-FX-90Q (90 MHz) spectrometers with tetramethylsilane as an internal standard. Mass (ms) spectra were recorded on a JEOL JMS-01SG mass spectrometer.

2-Methylthioimidazo[1,2-*a*]pyridine (**2a**).

A solution of 4.72 g (20 mmoles) of ethyl 2-methylthioimidazo[1,2-*a*]-pyridine-3-carboxylate (**1a**) [9,15] and 10% sodium hydroxide (sodium hydroxide 3.20 g, 80 mmoles) in 100 ml of methanol was refluxed 3 hours. After removal of the solvent and water, 20 g of polyphosphoric acid was added to the residue and the mixture was heated at 100° for 1 hour. The reaction mixture was poured into 300 ml of ice-water, neutralized with sodium carbonate and extracted with benzene (100 ml x 2). The combined extracts were dried over anhydrous sodium sulfate and evaporated *in vacuo*. The residue was chromatographed over alumina with a mixture of hexane-benzene (3:1) as an eluent to give 3.02 g (18.4 mmoles, 92%) of **2a** as an oil; ir (potassium bromide): ν max cm^{-1} 3180, 2925, 1635, 1469, 1327, 1293, 759; uv (ethanol): λ max nm (lot ϵ) 229 (4.28), 315 (3.74); ^1H nmr (deuteriochloroform): δ 2.55 (3H, s, SMe), 6.60-6.76 (1H, m, 6-H), 6.98-7.17 (1H, m, 7-H), 7.40 (1H, s, 3-H), 7.45 (1H, d, J = 10.2 Hz, 5-H), 7.94-8.04 (1H, m, 8-H); ms: m/z 164 (M^+, 100), 163 (43), 131 (46), 105 (22), 78 (71). This compound was used in the next reaction without further purification.

6,8-Dimethyl-2-methylthioimidazo[1,2-*a*]pyridine (**2b**).

This compound (1.75 g, 9.1 mmoles) was synthesized in 91% yield from ethyl 6,8-dimethyl-2-methylthioimidazo[1,2-*a*]pyridine-3-carboxylate (**1b**) (2.64 g, 10 mmoles) in a similar manner to that described for the preparation of **2b**; ^1H nmr (deuteriochloroform): δ 2.21 (3H, d, J = 1.1 Hz, 8-Me), 2.49 (6H, s, 5-Me and SMe), 5.82 (1H, s, 3, 5, or 7-H), 6.75 (1H, s, 3, 5, or 7-H), 7.64 (1H, s, 3, 5, or 7-H). This compound was used in the next reaction without further purification.

Dimethyl 2-Methylthio-1-azacycl[3.2.2]azine-3,4-dicarboxylate (**3a**).

A mixture of 2.50 g (15.2 mmoles) of **2a**, 2.0 g of 5% of palladium-on-charcoal catalyst, and 50 ml of toluene was refluxed 30 hours. After removal of the catalyst and solvent, the dark residual solid was taken up in 10 ml of methanol to give yellow crystals which were collected by filtration. This compound was recrystallized from methanol to give 1.68 g (5.53 mmoles, 36%) of yellow needles, mp 133°; ir (potassium bromide): ν max cm^{-1} 1741, 1710 (C=O); uv (ethanol): λ max nm (log ϵ) 267 (4.44), 340 (3.87), 392 (4.24), 410 (4.24); ^1H nmr (deuteriochloroform): δ 2.89 (3H, s, SMe), 4.03 (3H, s, OMe), 4.10 (3H, s, OMe), 7.76 (1H, dd, J = 1.2, 7.6 Hz, 7-H), 8.22 (1H, dd, J = 1.2, 7.6 Hz, 5-H), 7.96 (1H, t, J = 7.6 Hz, 6-H); ms: m/z 304 (M^+, 63), 272 (42), 214 (44), 196 (100).

Anal. Calcd. for $C_{14}H_{12}N_2O_4S$: C, 55.26; H, 3.97; N, 9.20; S, 10.54. Found: C, 55.25; H, 3.91; N, 9.30; S, 10.70.

Dimethyl 5,7-Dimethyl-2-methylthio-1-azacycl[3.2.2]azine-3,4-dicarboxylate (**3b**).

This compound (1.04 g, 3.12 mmoles) was synthesized in 40% yield from 1.50 g (7.8 mmoles) of **2b** in a similar manner to that described for the preparation of **3a**. An analytical sample was recrystallized from methanol to give yellow needles, mp 147°; ir (potassium bromide): ν max cm^{-1} 1725 (C=O); uv (ethanol): λ max nm (log ϵ) 216 (4.14), 255 (4.10), 293 (4.25), 346 (3.85), 404 (4.15); ^1H nmr (deuteriochloroform): δ 2.79 (3H, s, 5 or 7-Me), 2.83 (3H, s, 5 or 7-Me), 2.88 (3H, s, SMe), 4.01 (3H, s, OMe), 4.04 (3H, s, OMe), 7.45 (1H, s, 6-H); ms: m/z 332 (M^+, 100), 300 (85).

Anal. Calcd. for $C_{16}H_{16}N_2O_4S$: C, 57.82; H, 4.85; N, 8.43; S, 9.65. Found: C, 57.76; H, 4.86; N, 8.36; S, 9.83.

2-Methylthio-1-azacycl[3.2.2]azine (**4a**).

A solution of 1.85 g (6.1 mmoles) of **3a** in 100 ml of a 10% methanolic sodium hydroxide (sodium hydroxide, 1.92 g, 48 mmoles) solution was refluxed for 5 hours. After removal of the methanol under reduced pressure, the residual solid was dissolved in water and acidified. The solid was collected by filtration to give 1.64 g (5.9 mmoles, 97%) of orange crystals. This diacid must be used after drying by the vacuum pump. A mixture of 1.64 g of the crude diacid and 1.4 g of copper chromate catalyst in 30 ml of diphenyl ether was boiled under refluxed for 8 hours. The solution was then diluted with benzene and the catalyst was by filtration. The filtrate was extracted several times with 6*N* hydrochloric acid. After neutralization, the aqueous acid extract was extracted in turn with benzene. After removal of the orange layer, the residue was purified by alumina column chromatograph to give 0.48 g (2.56 mmoles, 42%) yellow oil; ir (potassium bromide): ν max cm^{-1} 3080, 2950, 1608, 1499, 1364, 789; uv (ethanol): λ max nm (log ϵ) 245 (4.41), 308 (4.09), 377 (4.25); ^1H nmr (deuteriochloroform): δ 2.92 (3H, s, SMe), 7.21 (1H, d, J = 4.4 Hz, 4-H), 7.53 (1H, d, J = 4.4 Hz, 3-H), 7.77-7.82 (3H, m, 5, 6, 7-H); ms: m/z 188 (M^+, 89), 155 (100), 143 (53), 63 (32).

Trinitrofluorenone complex, mp 161°, dark violet needles.

Anal. Calcd. for $C_{23}H_{13}N_5O_7S$: C, 54.88; H, 2.60; N, 13.91. Found: C, 54.43; H, 2.54; N, 13.97.

5,7-Dimethyl-2-methylthio-1-azacycl[3.2.2]azine (**4b**).

This compound (0.23 g, 1.06 mmoles) was synthesized in 44% yield from 0.80 g (2.4 mmoles) of **3b** in a manner similar to that described for the preparation of **4a**. Purification of the crude product by preparative tlc (hexane: benzene 1:1) yielded 2-methylthio-1-azacycl[3.2.2]azine (**4b**), mp 47°; ir (potassium bromide): ν max cm^{-1} 2920, 1490, 1362, 1342, 775; uv (ethanol): λ max nm (log ϵ) 225 (4.54), 249 (4.77), 316 (4.52), 372 (4.41); ^1H nmr (deuteriochloroform): δ 2.75 (3H, s, 5 or 7-Me), 2.84 (3H, s, 5 or 7-Me), 2.90 (3H, s, SMe), 7.15 (1H, d, J = 4.4 Hz, 4-H), 7.37 (1H, d, J = 4.4 Hz, 3-H), 7.39 (1H, s, 6-H); ms: m/z 216 (M^+, 100), 215 (37), 183 (95), 171 (14).

Picrate, mp 193°, yellow needles.

Anal. Calcd. for $C_{18}H_{15}N_5O_7S$: C, 48.54; H, 3.39; N, 15.72; S, 7.20. Found: C, 48.24; H, 3.35; N, 15.73; S, 7.08.

1-Azacycl[3.2.2]azine (**5a**).

A mixture of 0.43 g (2.29 mmoles) of **4a**, 0.8 g of Raney-nickel, and 30 ml of ethanol was refluxed for 6 hours. After removal of the Raney-nickel and solvent, the residue was chromatographed on an alumina-column using hexane as an eluent to give 0.11 g (0.77 mmoles, 34%) colorless oil. The picrate was yellow needles, mp 222° [lit [1] mp 220°]; ir (potassium bromide): ν max cm^{-1} 3100, 1610, 1502, 1342, 1182, 1138, 1040, 795; uv (ethanol): λ max nm (log ϵ) 226 (4.43), 235 (4.30), 282 (3.86), 287 (3.85),

291 (3.87), 368 (3.76), 378 (3.79); ^{1}H nmr (deuteriochloroform): δ 7.29 (1H, d, J = 4.6 Hz, 4-H), 7.58 (1H, d, J = 4.6 Hz, 3-H), 7.74-8.10 (3H, m, 5, 6, 7-H), 8.52 (1H, s, 2-H); ms: m/z 142 (M^+, 100), 115 (20).

5,7-Dimethyl-1-azacycl[3.2.2]azine (**5b**).

This compound (0.29 g, 1.71 mmoles) was synthesized in 85% yield from 0.43 g (2.0 mmoles) of **4b** in a manner similar to that described for **5a**. An analytical sample was recrystallized from methanol to give pale yellow needles, mp 106°; ir (potassium bromide): ν max cm^{-1} 3070, 1500, 1341, 790; uv (ethanol): λ max nm (log ε) 233 (4.52), 292 (4.06), 300 (4.11), 366 (3.98); ^{1}H nmr (deuteriochloroform): δ 2.82 (3H, s, 5 or 7-Me), 2.94 (3H, s, 5 or 7-Me), 7.29 (1H, d, J = 4.6 Hz, 4-H), 7.47 (1H, d, J = 4.6 Hz, 3-H), 7.52 (1H, s, 6-H), 8.36 (1H, s, 2-H); ms: m/z 170 (M^+, 100), 155 (25).

Anal. Calcd. for $C_{11}H_{10}N_2$: C, 77.62; H, 5.92; N, 16.46. Found: C, 77.71; H, 5.83; N, 16.49.

Picrate, mp 260°, yellow needles.

Anal. Calcd. for $C_{17}H_{13}N_5O_7$: C, 51.13; H, 3.28; N, 17.54. Found: C, 51.04; H, 3.17; N, 17.61.

2-Methylthioimidazo[2,1-*a*]isoquinoline (**7**).

This compound (9.50 g, 44.6 mmoles) was synthesized in 91% yield from 14.0 g (49.1 mmoles) of ethyl 2-methylthioimidazo[2,1-*a*]isoquinoline-3-carboxylate (**6**) in a manner similar to that described for **2a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 87°; ir (potassium bromide): ν max cm^{-1} 1365, 783; uv (ethanol): λ max nm (log ε) 238 (4.37), 245 (4.47), 265 (4.48); ^{1}H nmr (deuteriochloroform): δ 2.60 (3H, s, SMe), 7.22 (1H, d, J = 7.3 Hz, 6-H), 7.44 (1H, s, 3-H), 7.49-7.68 (3H, m, 7, 8, 9-H), 7.80 (1H, d, J = 7.3 Hz, 5-H); ms: m/z 214 (M^+, 100), 213 (22), 181 (84), 155 (16), 128 (39), 107 (13).

Anal. Calcd. for $C_{12}H_{10}N_2S$: C, 67.26; H, 4.70; N, 13.07; S, 14.96. Found: C, 67.47; H, 4.67; N, 12.94; S, 15.01.

Reaction of **7** with DMAD.

A mixture of 6.76 g (31.6 mmoles) of **7**, 6.30 g (45 mmoles) of DMAD, 5.0 g of palladium-on-charcoal, and 200 ml of toluene was refluxed for 30 hours. After removal of the palladium-on-charcoal and solvent, the residue was taken up in 15 ml of methanol. The yellow crystals that appeared were collected by filtration and recrystallized from methanol to give 2.77 g (9.80 mmoles, 31%) of dimethyl pyrrolo[2,1-*a*]isoquinoline-1,2-dicarboxylate (**9**) as yellow plates, mp 130°; ir (potassium bromide): ν max cm^{-1} 1735, 1705 (C=O); uv (ethanol): λ max nm (log ε) 264 (4.68), 323 (3.82); ^{1}H nmr (deuteriochloroform): δ 3.88 (3H, s, OMe), 4.04 (3H, s, OMe), 6.87 (1H, d, J = 7.5 Hz, 6-H), 7.40-7.57 (3H, m, 7, 8, 9-H), 7.65 (1H, d, J = 7.5 Hz, 5-H), 7.70 (1H, s, 3-H), 8.19-8.30 (1H, m, 10-H); ms: m/z 283 (M^+, 100), 253 (15), 252 (95), 139 (11).

Anal. Calcd. for $C_{18}H_{14}N_2O_4S$: C, 61.01; H, 3.98; N, 7.90; S, 9.05. Found: C, 60.75; H, 3.95; N, 7.88; S, 9.13.

The above filtrate was allowed to stand for 10 hours. The orange needles that appeared were collected by filtration and recrystallized from methanol to give 0.57 g (1.6 mmoles, 5.1%) of **8**, mp 132°; ir (potassium bromide): ν max cm^{-1} 1730, 1705 (C=O); uv (ethanol): λ max nm (log ε) 258 (4.38, shoulder), 275 (4.64), 366 (3.83), 444 (4.16), 468 (4.06); ^{1}H nmr (deuteriochloroform): δ 2.97 (3H, s, SMe), 4.08 (3H, s, OMe), 4.13 (3H, s, OMe), 7.69-7.92 (2H, m, 7, 8-H), 8.21-8.32 (1H, m, 6-H), 8.60 (1H, s, 5-H), 8.80-8.91 (1H, m, 9-H); ms: m/z 354 (M^+, 44), 283 (51), 252 (100), 81 (36), 69 (66).

Anal. Calcd. for $C_{18}H_{14}N_2O_4S$: C, 61.01; H, 3.98; N, 7.90; S, 9.05. Found: C, 60.75; H, 3.95; N, 7.33; S, 9.13.

After removal solvent of the filtrate, the residue was chromatographed on alumina column using hexane:benzene (3:1) as an eluent to give 0.45 g (1.26 mmoles, 4%) of methyl (2-methylthioimidazo[2,1-*a*]isoquinol-3-yl)-α-methoxycarbonylacrylate (**10**) as yellow needles, mp 135°, ir (potassium bromide): ν max cm^{-1} 1725, 1695 (C=O); uv (ethanol): λ max nm (log ε) 250 (4.39, shoulder), 266 (4.51), 290 (4.19, shoulder), 367 (4.03); ^{1}H nmr (deuteriochloroform): δ 2.74 (3H, s, SMe), 3.83 (3H, s, OMe), 3.93 (3H, s, OMe), 6.30 (1H, s, vinyl-H), 7.09 (1H, d, J = 7.5 Hz, 6-H), 7.56-7.72 (3H, m, 7, 8, 9-H), 7.94 (1H, d, J = 7.5 Hz, 5-H), 8.61-8.71 (1H, m, 10-H); ms: m/z 356 (M^+, 45), 297 (36), 283 (96), 252 (100), 128 (25), 69 (40).

Anal. Calcd. for $C_{18}H_{16}N_2OS$: C, 60.66; H, 4.53; N, 7.86; S, 9.00. Found: C, 60.82; H, 4.35; N, 7.24; S, 8.87.

Subsequent elution using hexane:benzene (1:1) as the eluent gave a mixture of **8** and **9** which are separated by recrystallization from methanol to give 0.099 g (0.28 mmole, 0.9%) of **8** and 0.178 g (0.63 mmole, 2%) of **9**. Subsequent elution using benzene as the eluent gave tetramethyl 1,11b-dihydro-2-methylthio-1-azabenzo[*g*]cycl[4,3,2]azine-3,4,5,6-tetracarboxylate (**11**) as colorless prisms, mp 207°; ir (potassium bromide): ν max cm^{-1} 1710 (C=O); uv (ethanol): λ max nm (log ε) 220 (4.22), 230 (4.21), 250 (4.24), 282 (3.79); ^{1}H nmr (deuteriochloroform): δ 2.55 (3H, s, SMe), 3.67 (3H, s, OMe), 3.93 (3H, s, OMe), 3.97 (3H, s, OMe), 3.98 (3H, s, OMe), 7.07 (1H, d, J = 3.1 Hz, 12-H), 7.49-7.84 (4H, m, 8, 9, 10-H), 8.21 (1H, s, 7-H), 10.94 (1H, bs, NH); ms: m/z 498 (M^+, 80), 450 (56), 419 (80), 69 (62), 57 (100).

Anal. Calcd. for $C_{24}H_{22}N_2O_8S$: C, 57.82; H, 4.45; N, 5.62; S, 6.43. Found: C, 57.81; H, 4.43; N, 5.42; S, 6.41.

2-Methylthio-1-azabenzo[*h*]cycl[3.2.2]azine (**12**).

This compound (0.41 g, 1.7 mmoles) was synthesized in 34% yield from 1.77 g (5 mmoles) of **8** in a manner similar to that described for the preparation of **4a**. An analytical sample was recrystallized from methanol to give **12** as yellow needles, mp 113°; ir (potassium bromide): ν max cm^{-1} 1487, 1385, 1270, 1235, 750; uv (ethanol): λ max nm (log ε) 219 (4.16), 240 (4.20, shoulder), 257 (4.50), 261 (4.51), 280 (4.48), 297 (4.28, shoulder), 398 (4.05), 416 (4.17); ^{1}H nmr (deuteriochloroform): δ 2.94 (3H, s, SMe), 7.30 (1H, d, J = 4.8 Hz, 4-H), 7.63 (1H, d, J = 4.8 Hz, 3-H), 7.69-7.88 (2H, m, 7, 8-H), 8.11 (1H, s, 5-H), 8.16-8.27 (1H, m, 6-H); ms: m/z 238 (M^+, 84), 205 (100), 71 (27), 57 (46), 55 (24).

Anal. Calcd. for $C_{14}H_{10}N_2S$: C, 70.56; H, 4.23; N, 11.75; S, 13.46. Found: C, 70.66; H, 4.17; N, 11.50; S, 13.42.

1-Azabenzo[*h*]cycl[3.2.2]azine (**13**).

This compound (0.045 g, 0.23 mmole) was synthesized in 15% yield from 0.38 g (1.6 mmoles) of **12** in a manner similar to that described for the preparation of **5a**. An analytical sample was recrystallized from methanol to give **13** as pale yellow prisms, mp 90°; ir (potassium bromide): ν max cm^{-1} 1485, 1385, 1110, 1040, 835, 745, 660; uv (ethanol): λ max nm (log ε) 225 (4.12, shoulder), 257 (4.62), 266 (4.52), 276 (4.40), 292 (3.92), 304 (3.94), 317 (3.94), 322 (3.92, shoulder), 331 (3.90), 385 (3.63), 404 (3.63); ^{1}H nmr (deuteriochloroform): δ 7.40 (1H, d, J = 5.0 Hz, 4-H), 7.68 (1H, d, J = 5.0 Hz, 3-H), 7.75-7.97 (2H, m, 7, 8-H), 8.21 (1H, s, 5-H), 8.26 (1H, s, 2-H), 8.21-8.32 (1H, m, 6-H), 8.92-9.04 (1H, m, 9-H); ms: m/z 192 (M^+, 100), 164 (12), 96 (11).

Anal. Calcd. for $C_{13}H_8N_2$: C, 81.23; H, 4.20; N, 14.57. Found: C, 81.45; H, 4.07; N, 14.62.

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