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Reaction of 2-Bis(methylthio)methyleneindan-1,3-dione with N-Ylides and S-Ylides

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The reaction of **1** with pyridinium N-ylides (**2a**, R = H; **2b**, R = 3-CH_3; **2c**, R = 2-CH_3; and **2d**, R = 2-NH_2) gave the corresponding stable pyridinium N-allylide compounds (**3a** and **3b**), 2-(2-indanyl)indolizine (**4**), and 3-(2-indanylidenyl)methylimidazo[1,2-*a*]pyridine (**5**) in good yields. A fused thiabenzene oxide, 2-methyl-4-methylthio-5-oxo-5*H*-indeno[1,2-*c*]thiapyran 2-oxide (**8**), was synthesized by the reaction of **1** with trimethylsulfoxonium iodide under similar conditions. An azathiabenzene oxide, 2-methyl-4-methylthio-5-oxo-5*H*-indeno[2,1-*d*][1,2]thiazine 2-oxide (**11**), was also synthesized from 2-(1-dimethylsulfoximino-1-methylthio)methyleneindan-1,3-dione (**10**), which was prepared from **1** and sulfoximine.

Keywords——ketenethioacetal; 1,3-indadione; pyridinium N-ylide; indolizine; thiabenzene oxide; S-ylide; azathiabenzene oxide; pyrimidine; imidazo[1,2-*a*]pyridine

It is well known that ketenethioacetals react with active methylene compounds of various types, giving the corresponding mono-substituted products and heterocyclic compounds.[1] We have previously reported the reaction of 2-bis(methylthio)methyleneindan-1,3-dione (**1**) with active methyl or methylene compounds, giving the corresponding indan derivatives.[2]

The present paper describes the reaction of **1** with pyridinium N-ylides, S-ylides, and S-imine. Recently, we reported the synthesis of stable pyridinium N-allylides and indolizine derivatives using the reaction of ketenethioacetals with various N-ylides.[3] We have now applied the above reaction to the preparation of new N-ylide compounds. The reaction of **1** with 1-ethoxycarbonylmethylpyridinium bromide (**2a**: R = H, **2b**: R = CH_3) in the presence of triethylamine in ethanol gave the corresponding stable pyridinium N-ylides (**3a** and **3b**) in 52 and 77% yields, respectively. Compound **1** was also reacted with 1-ethoxycarbonylmethyl-2-methylpyridinium bromide (**2c**) in the presence of potassium carbonate in *N,N*-dimethylformamide to give 2-(3-ethoxycarbonylindolizin-2-yl)indan-1,3-dione (**4**) in 72% yield. When **1** was reacted with 2-amino-1-ethoxycarbonylmethylpyridinium bromide (**2d**) under the same conditions, 2-(2-hydroxyimidazo[1,2-*a*]pyrid-3-yl) (methylthio)methyleneindan-1,3-dione (**5**) was obtained in 86% yield.

The synthesis of monocyclic 1-methylthiabenzene 1-oxides and 1-methyl-2-azathiabenzene 1-oxides *via* the reaction of ketenethioacetals was first reported by Furukawa *et al.*[4] Previous investigations of the synthesis of thiabenzene 1-oxides have dealt almost exclusively with monocyclic compounds. However, the present investigation of ketenethioacetals was undertaken in order to obtain fused thiabenzene oxides and azaznalogs having an indene ring.

The reaction of **1** with trimethylsulfoxonium iodide[5] in the presence of sodium hydride in tetrahydrofuran gave a thiabenzene oxide, 2-methyl-4-methylthio-5-oxo-5*H*-indeno[1,2-*c*]thiapyran 2-oxide (**8**), in 30% yield. Treatment of an N-substituted dimethyl sulfoximine, *N*-[1,3-dioxoindan-2-ylidene-α-methylthio)methyl]dimethylsulfoximine (**10**), which was pre-

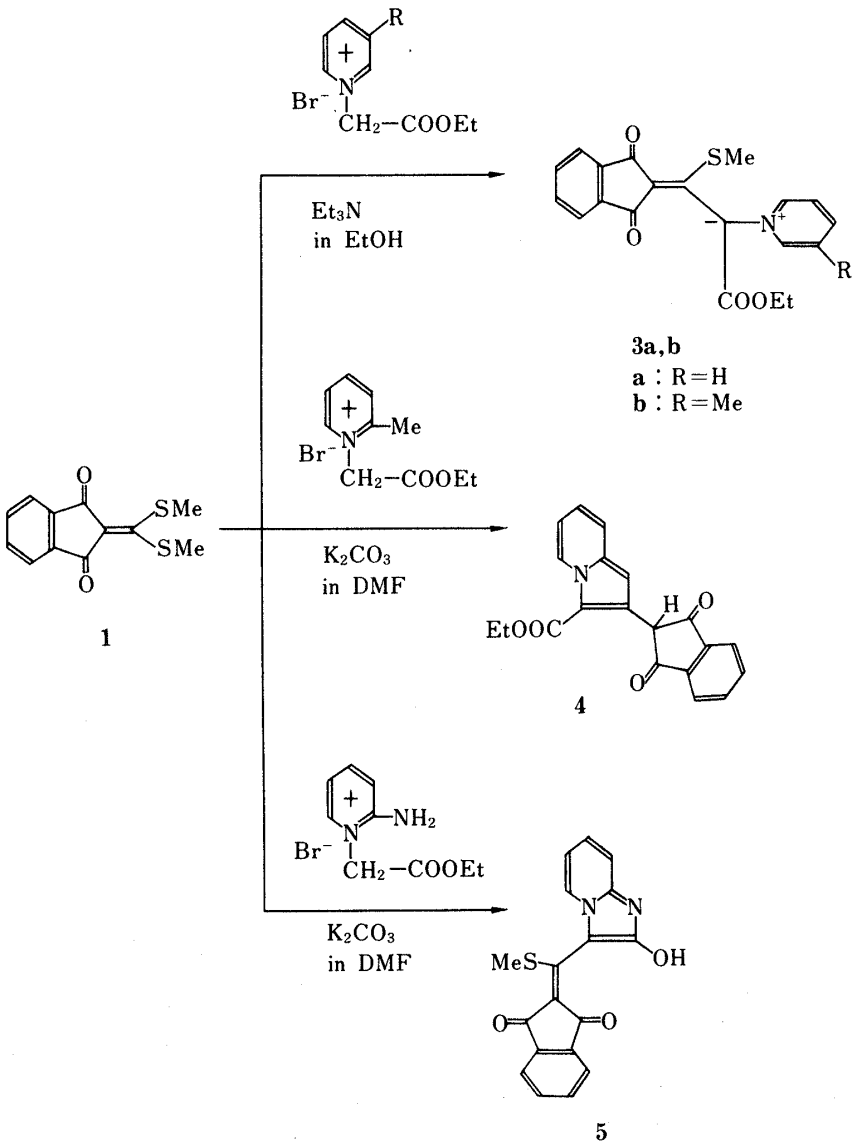
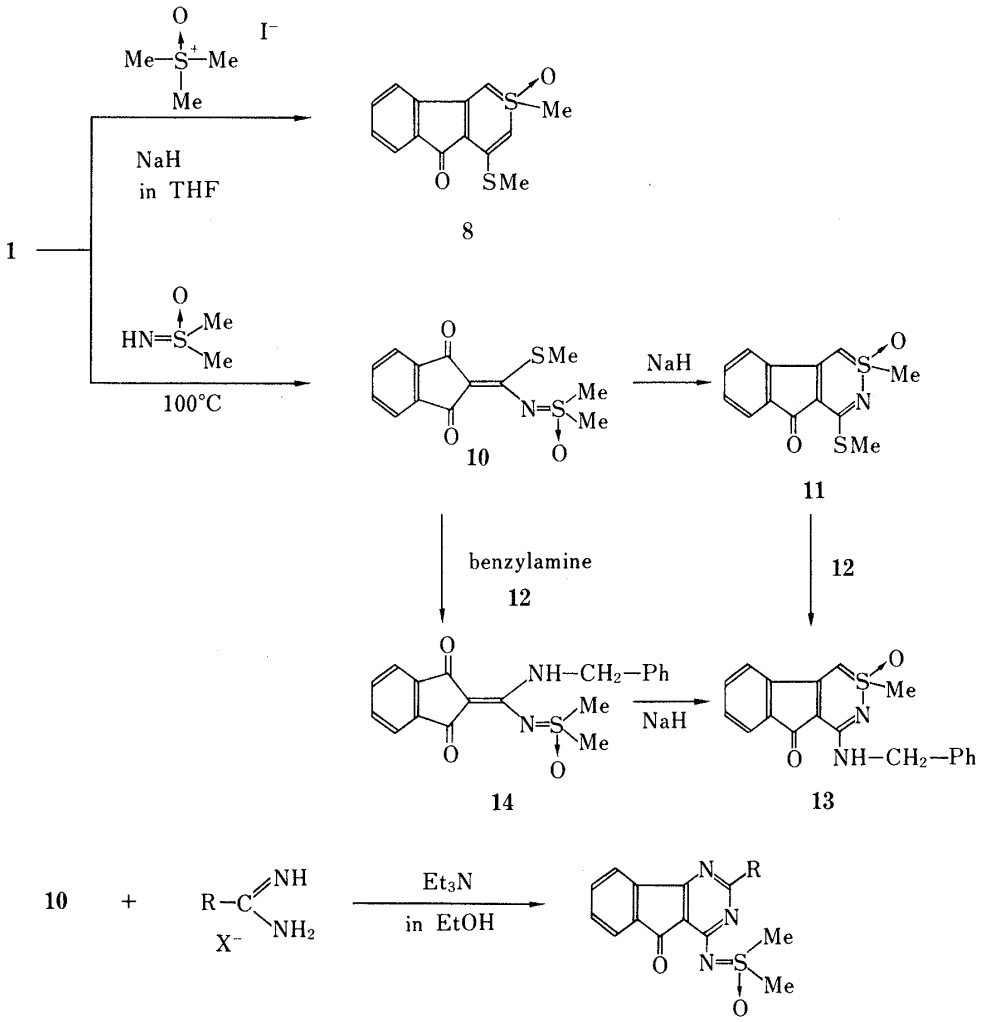


Chart 1

pared by the reaction of **1** with dimethylsulfoximine,[6] with sodium hydride in tetrahydrofuran (THF) afforded an azathiabenzene oxide, 2-methyl-4-methylthio-5-oxo-5*H*-indeno[2,1-*d*] [1,2]thiazine 2-oxide (**11**), in 45% yield (from **10**). Compound **11** was reacted with benzylamine (**12**) to give the displacement product of the methylthio group, 4-benzylamino-2-methyl-5-oxo-5*H*-indeno[2,1-*d*] [1,2]thiazine 2-oxide (**13**), in 74% yield. This compound **13** was also synthesized from **14**, which was prepared by the reaction of **10** with benzylamine, in a manner similar that used for the preparation of **11** from **10**.

In recent years, the synthesis of pyrimidine derivatives by using the reaction of ketenethioacetals has been reported by several groups.[7] We applied the above reaction to the preparation of indeno[1,2-*d*]pyrimidine derivatives. The reaction of **1** with acetamidine hydrochloride in the presence of triethylamine in ethanol gave 2-methyl-4-dimethylsulfoximino-5-oxo-5*H*-indeno[1,2-*d*]pyrimidine (**16a**) in 42% yield. In a similar manner, other 2-substituted 5-oxo-5*H*-indeno[1,2-*d*]pyrimidines (**16b**, **16c**, and **16d**) were also easily obtained by the reaction of **1** with amidine compounds (*S*-methylisothiourea sulfate, *S*-benzylisothiourea hydrochloride, guanidine carbonate) in good yields.



15a,b,c,d

a : R=Me, X=Cl
b : R=SMe, X=HSO_4
c : R=SCH_2-Ph, X=Cl
d : R=NH_2, X=HCO_3

16a,b,c,d

a : R=Me
b : R=SMe
c : R=SCH_2-Ph
d : R=NH_2

Chart 2

Experimental

All melting points were determined in a capillary tube and are uncorrected. Infrared (IR) spectra were recorded in KBr pellets on a JACO IRA-2 spectrometer, ultraviolet (UV) absorption spectra were determined in 95% EtOH on a Hitachi EP-S2 spectrometer, and nuclear magnetic resonance (NMR) spectra were obtained on a JNM-PS-100 (100 MHz) spectrometer with tetramethylsilane as an internal standard. Mass spectra (MS) were recorded on a JEOL JMS-01SG mass spectrometer.

(Ethoxycarbonyl)[1,3-dioxoindan-2-ylidene)(methylthio)methyl](1-pyridinio)methylide (3a)——A solution of 0.5 g (2 mmol) of **1**, 0.45 g (2 mmol) of 1-ethoxycarbonylmethylpyridinium bromide (**2a**), and 5 ml of triethylamine in 20 ml of EtOH was refluxed on a boiling water bath for 1 h. Half the solvent was evaporated off. The remaining solution was cooled, and the precipitate was collected by filtration then recrystallized from ethanol to give 0.38 g (52%) of yellow needles, mp 232 °C (dec.). IR ν(KBr) cm^{-1}: 1692, 1653 (C=O). UV λ_{max}^{EtOH} nm (log ε): 251 (4.46), 310 (4.05), 364 (4.03). NMR ($CDCl_3$) δ: 1.28 (3H, t, J=7 Hz, CH_2–$\underline{CH_3}$), 2.35 (3H, s, SCH_3), 4.26 (2H, q, J=7 Hz, $\underline{CH_2}$–CH_3), 7.32 (4H, s, aromatic protons on indan ring), 7.70 (2H, dd, J=7, 8 Hz, 3, 5-H on pyridine ring), 8.19 (1H, t, J=8 Hz, 4-H on pyridine ring), 8.74 (2H, dd, J=1, 7 Hz, 2, 6-H on pyridine ring). MS m/e: 367 (M^+), 320 (M^+-47), 288. *Anal.* Calcd for $C_{20}H_{17}NO_4S$: C, 65.38; H, 4.66; N, 3.81; S, 8.73. Found: C, 65.21; H, 4.71; N, 3.72; S, 8.53.

(Ethoxycarbonyl)[1,3-dioxoindan-2-ylidene)(methylthio)methyl](3-methyl-1-pyridinio)methylide (3b)——This compound was synthesized from **1** and 1-ethoxycarbonyl-3-methylpyridinium bromide (**2b**) in a manner similar to

that described for the preparation of **3a**, in 77% yield. An analytical sample was recrystallized from C_6H_6–EtOH to give yellow plates, mp 252 °C (dec.). IR ν(KBr) cm^{-1}: 1692, 1653 (C=O). UV λ_{max}^{EtOH} nm (log ε): 252 (4.46), 311 (4.06), 366 (4.00). NMR ($CDCl_3$) δ: 1.28 (3H, t, J=7 Hz, CH_2–CH_3), 2.37 (3H, s, SCH_3), 2.43 (3H, s, 3-CH_3 on pyridine ring), 4.27 (2H, q, J=7 Hz, CH_2–CH_3), 7.31 (4H, s, aromatic protons on indan ring), 7.60 (1H, dd, J=7, 8 Hz, 5-H on pyridine ring), 7.91 (1H, br d, J=8 Hz, 4-H on pyridine ring), 8.44 (1H, br s, 2-H on pyridine ring), 8.45 (1H, br d, J=7 Hz, 6-H on pyridine ring). *Anal.* Calcd for $C_{21}H_{19}NO_4S$: C, 66.12; H, 5.02; N, 3.67; S, 8.41. Found: C, 65.58; H, 4.99: N, 3.53; S, 8.48.

Ethyl 2-(1,3-Dioxoindan-2-yl)indolizine-3-carboxylate (4)——A mixture of 0.5 g (2 mmol) of **1**, 0.52 g (2 mmol) of 1-ethoxycarbonylmethyl-2-methylpyridinium bromide (**2c**), 0.55 g (4 mmol) of potassium carbonate, and 15 ml of dimethylformamide (DMF) was stirred at room temperature for 3 h, then was poured into 100 ml of water and acidified with 10% HCl. The precipitate was collected by filtration and recrystallized from EtOH to give 0.48 g (72%) of reddish-violet needles, mp 190 °C (dec.). IR ν(KBr) cm^{-1}: 3420 (OH), 1748, 1717, 1663 (C=O). UV ν_{max}^{EtOH} nm (log ε): 221 (4.66), 254 (4.50), 296 (4.39), 338 (4.20). NMR ($CDCl_3$) δ: 0.83 (3H, t, J=7 Hz, CH_2–CH_3), 3.70 (2H, q, J=7 Hz, CH_2–CH_3), 4.73 (1H, s, 2-H on indan ring), 6.73 (1H, s, 1-H), 6.78 (1H, dd, J=7, 8 Hz, 6-H), 7.03 (1H, dd, J=8, 8 Hz, 7-H), 7.46 (1H, near d, J=8 Hz, 8-H), 7.82—8.14 (4H, m, indan ring protons), 9.34 (1H, d, J=7 Hz, 5-H). *Anal.* Calcd for $C_{20}H_{15}NO_4$: C, 72.06; H, 4.54; N, 4.20. Found: C, 71.69; H, 4.60; N, 4.12.

2-(2-Hydroxyimidazo[1,2-*a*]pyrid-3-yl)(methylthio)methyleneindan-1,3-dione (5)——A mixture of 0.5 g (2 mmol) of **1**, 0.52 g (2 mmol) of 2-amino-1-ethoxycarbonylmethylpyridinium bromide (**2d**), 0.55 g (4 mmol) of potassium carbonate, and 15 ml of DMF was stirred at room temperature for 3 h, then poured into 100 ml of water and acidified with 10% HCl. The precipitate was collected by filtration and recrystallized from C_6H_6–MeOH to give 0.58 g (86%) of red needles, mp 292 °C (dec.). IR ν(KBr) cm^{-1}: 1628, 1656 (C=O). UV λ_{max}^{EtOH} nm (insufficient solubility): 245, 306, 384, 483; λ_{min}: 229, 283. NMR (DMSO-d_6) δ: 2.55 (3H, s, SCH_3), 7.04 (1H, dd, J=6.6, 7.2 Hz, 6-H), 7.30 (1H, d, J=7.2 Hz, 8-H), 7.60 (4H, s, indan ring protons), 7.66 (1H, dd, J=7.2, 7.2 Hz, 7-H), 8.11 (1H, d, J=6.6 Hz, 5-H). *Anal.* Calcd for $C_{18}H_{12}N_2O_3S$: C, 64.27; H, 3.60; N, 8.33; S, 9.53. Found: C, 64.34; H, 3.58; N, 8.26; S, 9.46.

2-Methyl-4-methylthio-5-oxo-5*H*-indeno[1,2-*c*]thiapyran 2-Oxide (8)——A mixture of 0.5 g (2 mmol) of **1**, 0.19 g (4 mmol) of NaH, 1.55 g (8 mmol) of trimethylsulfoxonium iodide (**7**),[5] and 20 ml of anhydrous THF was refluxed for 3 h. After evaporation of the solvent, 100 ml of water was added to the residue. The precipitate was collected by filtration and recrystallized from MeOH to give 0.16 g (30%) of yellow needles, mp 265 °C (dec.). IR ν(KBr) cm^{-1}: 1652 (C=O). UV λ_{max}^{EtOH} nm (log ε): 242 (4.56), 271 (4.32), 327 (4.11), 347 (3.82), 364 (3.60), 4.20 (3.30). NMR (DMSO-d_6) δ: 2.40 (3H, s, SCH_3), 3.74 (3H, s, 2-CH_3), 5.95 (1H, d, J=4 Hz, 3-H), 6.91 (1H, d, J=4 Hz, 1-H), 7.40—7.76 (4H, m, protons of indan ring). MS *m/e*: 276 (M^+, 100), 261 (M^+-15), 245, 233, 218, 156. *Anal.* Calcd for $C_{14}H_{12}O_2S_2$: C, 60.84; H, 4.38; S, 23.20. Found: C, 60.93; H, 4.31; S, 23.28.

2-[(Dimethylsulfoximino)(methylthio)methylene]indan-1,3-dione (10)——A mixture of 0.5 g (2 mmol) of **1** and 0.56 g (6 mmol) of sulfoximine[6] was heated at 100 °C for 30 min, then cooled. The reaction product was recrystallized from MeOH to give 0.4 g (76%) of pale yellow needles, mp 194 °C. IR ν(KBr) cm^{-1}: 1645 (C=O). UV λ_{max}^{EtOH} nm (log ε): 233 (4.40), 242 (4.38), 294 (3.94), 303 (4.03), 364 (4.39). NMR ($CDCl_3$) δ: 2.47 (3H, s, SMe), 3.40 (6H, s, $SOCH_3$), 7.54—7.78 (4H, m, 6, 7, 8, 9-H). *Anal.* Calcd for $C_{13}H_{13}NO_3S$: C, 52.86; H, 4.44; N, 4.74; S, 21.71. Found: C, 52.62; H, 4.40; N, 4.65; S, 21.60.

2-Methyl-4-methylthio-5-oxo-5*H*-indeno[2,1-*d*][1,2]thiazine 2-Oxide (11)——A mixture of 0.35 g (2 mmol) of **10**, 0.192 g (50%, 4 mmol) of NaH and 10 ml of anhydrous THF was refluxed for 3 h, then cooled. The reaction mixture was poured into 100 ml of ice-water. The precipitate was collected by filtration and recrystallized from C_6H_6–MeOH to give 0.255 g (45%) of yellow needles, mp 282 °C (dec.). IR ν(KBr) cm^{-1}: 1660 (C=O). UV λ_{max}^{EtOH} nm (insufficient solubility): 259, 322, 353; λ_{min}: 223, 300, 328. NMR (DMSO-d_6) δ: 2.45 (3H, s, SCH_3), 3.65 (3H, s, 2-CH_3), 7.18 (1H, s, 1-H), 7.59—7.95 (4H, m, 6, 7, 8, 9-H). *Anal.* Calcd for $C_{13}H_{11}NO_2S_2$: C, 56.30; H, 4.00; N, 5.05; S, 23.12. Found: C, 56.05; H, 4.12; N, 5.12; S, 23.46.

4-Benzylamino-2-methyl-5-oxo-5*H*-indeno[2,1-*d*][1,2]thiazine 2-Oxide (13)——a) A mixture of 0.49 g (2 mmol) of **11** and 0.43 g (4 mmol) of benzylamine was heated at 150 °C for 1 h, then cooled. The product was recrystallized from MeOH to give 0.5 g (74%) of yellow leaflets, mp 178 °C. b) This compound was also synthesized from **14** in a manner similar to that described for the preparation of **11** from **10**. The yield was 51%. IR ν(KBr) cm^{-1}: 3040 (NH), 1646 (C=O). UV λ_{max}^{EtOH} nm (log ε): 239 (4.55), 250 (4.56), 290 (4.13), 311 (4.28), 326 (4.14), 340 (4.02), 410 (3.72). NMR (DMSO-d_6) δ: 3.50 (3H, s, 2-CH_3), 4.66 (2H, d, J=6.4 Hz, N–CH_2–), 6.83 (1H, s, 1-H), 7.34 (5H, s, phenyl protons), 7.38—7.83 (4H, m, 6, 7, 8, 9-H), 8.50 (1H, br t, J=6.4 Hz, NH). *Anal.* Calcd for $C_{19}H_{16}N_2O_2S$: C, 67.84; H, 4.79; N, 8.33; S, 9.53. Found: C, 67.57; H, 4.70; N, 8.22; S, 9.59.

2-[(Benzylamino)(dimethylsulfoximino)methylene]indan-1,3-dione (14)——A mixture of 0.53 g (2 mmol) of **10** and 0.43 g (4 mmol) of benzylamine was heated at 150 °C for 30 min, then cooled. The product was recrystallized from MeOH to give 0.53 g (75%) of yellow needles, mp 169 °C. IR ν(KBr) cm^{-1}: 3000 (NH), 1670, 1620 (C=O). UV λ_{max}^{EtOH} nm (log ε): 226 (4.54), 293 (4.53), 320 (4.37), 332 (4.50). NMR (DMSO-d_6) δ: 3.43 (6H, s, $SOCH_3$), 4.66 (2H, d, J=6.1 Hz, N–CH_2–), 7.35 (5H, s, phenyl protons), 7.42—7.58 (4H, m, 4, 5, 6, 7-H), 10.15 (1H, br s, NH). *Anal.* Calcd for $C_{19}H_{18}N_2O_3S$: C, 64.39; H, 5.12; N, 7.90; S, 9.05. Found: C, 64.19; H, 5.18; N, 8.02; S, 8.94.

2-Methyl-4-dimethylsulfoximino-5-oxo-5*H*-indeno[1,2-*d*]pyrimidine (16a)——A mixture of 0.53 g (2 mmol) of **10**,

0.28 g (3 mmol) of acetamidine hydrochloride, 5 ml of triethylamine and 20 ml of EtOH was heated at reflux for 5 h. After evaporation of the solvent and excess triethylamine, 100 ml of water was added to the residue. The precipitate was collected by filtration and recrystallized from MeOH to give 0.24 g (42%) of yellow needles, mp 305 °C (dec.). IR ν(KBr) cm^{-1}: 1703 (C=O). UV λ_{max}^{EtOH} nm (insufficient solubility): 243, 283; λ_{min}: 224, 256. NMR (DMSO-d_6) δ: 2.57 (3H, s, 2-CH_3), 3.55 (6H, s, $SOCH_3$), 7.60—7.75 (4H, m, 6, 7, 8, 9-H). *Anal.* Calcd for $C_{14}H_{13}N_3O_2S$: C, 58.52; H, 4.56; N, 14.62; S, 11.16. Found: C, 58.72; H, 4.58; N, 14.38; S, 11.09.

4-Dimethylsulfoximino-2-methylthio-5-oxo-5*H*-indeno[1,2-*d*]pyrimidine (16b)——This compound was synthesized from **10** and *S*-methylisothiourea sulfate in a manner similar to that described for the preparation of **16a**, in 23% yield. An analytical sample was recrystallized from MeOH to give yellow needles, mp 270 °C (dec.). IR ν(KBr) cm^{-1} 1694 (C=O). UV λ_{max}^{EtOH} nm (log ε): 246 (4.57), 297 (4.69). NMR ($CDCl_3$) δ: 2.64 (3H, s, SCH_3), 3.50 (6H, s, $SOCH_3$), 7.46—7.87 (4H, m, 6, 7, 8, 9-H). *Anal.* Calcd for $C_{14}H_{13}N_3O_2S_2$: C, 52.65; H, 4.10; N, 13.16; S, 20.08. Found: C, 52.61; H, 4.05; N, 13.18; S, 19.85.

2-Benzylthio-4-dimethylsulfoximino-5-oxo-5*H*-indeno[1,2-*d*]pyrimidine (16c)——This compound was synthesized from **10** and *S*-benzylisothiourea hydrochloride in a manner similar to that described for the preparation of **16a**, in 41% yield. An analytical sample was recrystallized from MeOH to give yellow needles, mp 226 °C. IR ν(KBr) cm^{-1}: 1694 (C=O). UV λ_{max}^{EtOH} nm (log ε): 247 (4.57), 297 (4.70). NMR (DMSO-d_6) δ: 3.49 (6H, s, $SOCH_3$), 4.51 (2H, s, SCH_2–), 7.25—7.82 (9H, m, phenyl protons and 6, 7, 8, 9-H). *Anal.* Calcd for $C_{20}H_{17}N_3O_2S_2$: C, 60.74; H, 4.33; N, 10.62; S, 16.21. Found: C, 60.43; H, 4.37; N, 10.50; S, 16.08.

2-Amino-4-dimethylsulfoximino-5-oxo-5*H*-indeno[1,2-*d*]pyrimidine (16d)——This compound was synthesized from **10** and guanidine carbonate in a manner similar to that described for the preparation of **16a**, in 74% yield. An analytical sample was recrystallized from EtOH to give yellow plates, mp 312 °C. IR ν(KBr) cm^{-1}: 1646 (C=O). UV λ_{max}^{EtOH} nm (log ε): 239 (4.55), 250 (4.56), 290 (4.13), 311 (4.28), 326 (4.14), 340 (4.02), 410 (3.72). NMR (DMSO-d_6) δ: 3.51 (6H, s, $SOCH_3$), 7.50 (2H, br s, NH_2), 7.52—7.62 (4H, m, 6, 7, 8, 9-H). *Anal.* Calcd for $C_{19}H_{16}N_2O_2S$: C, 67.84; H, 4.79; N, 8.33; S, 9.53. Found: C, 67.57; H, 4.70; N, 8.22; S, 9.53.

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