Sulfonium ylides

7.* Influence of substituents in the imide fragment on the regioselectivity of intramolecular cyclization of phthalimido-containing keto-stabilized sulfonium ylides

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The intramolecular cyclization of keto-stabilized sulfonium ylides obtained from β-alanine and containing various imide fragments was studied. On heating in toluene in the presence of $PhCO_2H$, ylides containing a phthalimide moiety are converted into indolizidine-2,6-dione derivatives, whereas those incorporating a 4-methyl-1,2,3,6-tetrahydrophthalimide or pyrrolidine-2,5-dione moieties do not undergo cyclization.

Key words: keto-stabilized sulfonium ylides, intramolecular cyclization; indolizidine-2,6-dione, sulfur-containing derivatives

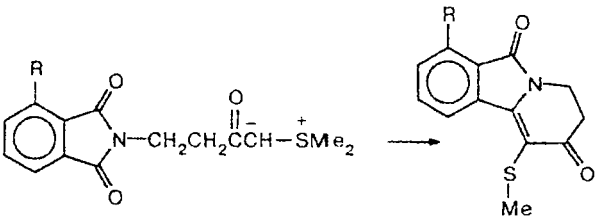
In continuation of the studies dealing with the intramolecular cyclization that we discovered for phthalimido-containing keto-stabilized sulfonium ylides prepared from α- and β-amino acids,[1–5] we discuss the results of a study of the effect of the structures of the imide fragments and the substituents present in them on the behavior of sulfonium ylides (**10—12**, **16**, **20**) obtained from β-alanine (Scheme 1).

Even during the synthesis of sulfonium ylides, which was carried out by the procedures described previously,[6] it became obvious that the nature and the position of the substituent in the phthalimide fragment are significant. For example, when a chlorine atom is present at position 3 of the phthalimide fragment, sulfonium ylide **11** is formed in almost quantitative yield, whereas in the presence of an NO_2 group in the same position, the yield of ylide **10** is only 12%. Deprotonation of salt **9** results in the formation of ylide **12** in a yield of 62%. Ylide **16** containing a tetrahydrophthalimide fragment instead of the phthalimide fragment is formed in a yield of 85%, while the yield of the ylide containing a succinimide fragment (**20**) does not exceed 55%.

Previously we showed that heating the sulfonium ylide, prepared from *N*-phthalyl-β-alanine, in toluene in the presence of an equimolar amount of benzoic acid affords a compound with an indolizidinedione structure.[1]

The introduction of a substituent into the phthalimide fragment of the sulfonium ylide molecule makes it possible to prepare the corresponding indolizidinediones as pairs of structural isomers. However, due to the nonequivalence of the carbonylphthalimide fragment (Table 1), one of the cyclization pathways predominates, and thus, one of the isomers is obtained as the only or the major product.

In fact, cyclization of sulfonium ylides **10** and **11** having substituents in position 3 of the phthalimide fragment occurs regioselectively to give compounds **21** and **22**, respectively.



10: R = NO_2
11: R = Cl

21: R = NO_2
22: R = Cl

The nitro group in position 4 of the phthalimide fragment of ylide **12** has no significant effect on the cyclization pathway, and isomers **23** and **24** are formed in approximately equal amounts.

Comparison of the ^{13}C NMR spectra of compounds **21**, **22**, and **23**, **24** with the spectrum of the indolizidinedione having no substituents in the benzene ring makes it possible to establish unambiguously the positions of the chlorine atom and the nitro group in the aromatic nucleus of the reaction products.[4]

The positions of substituents in the benzene ring can also be determined using ^1H NMR spectra. The signal of

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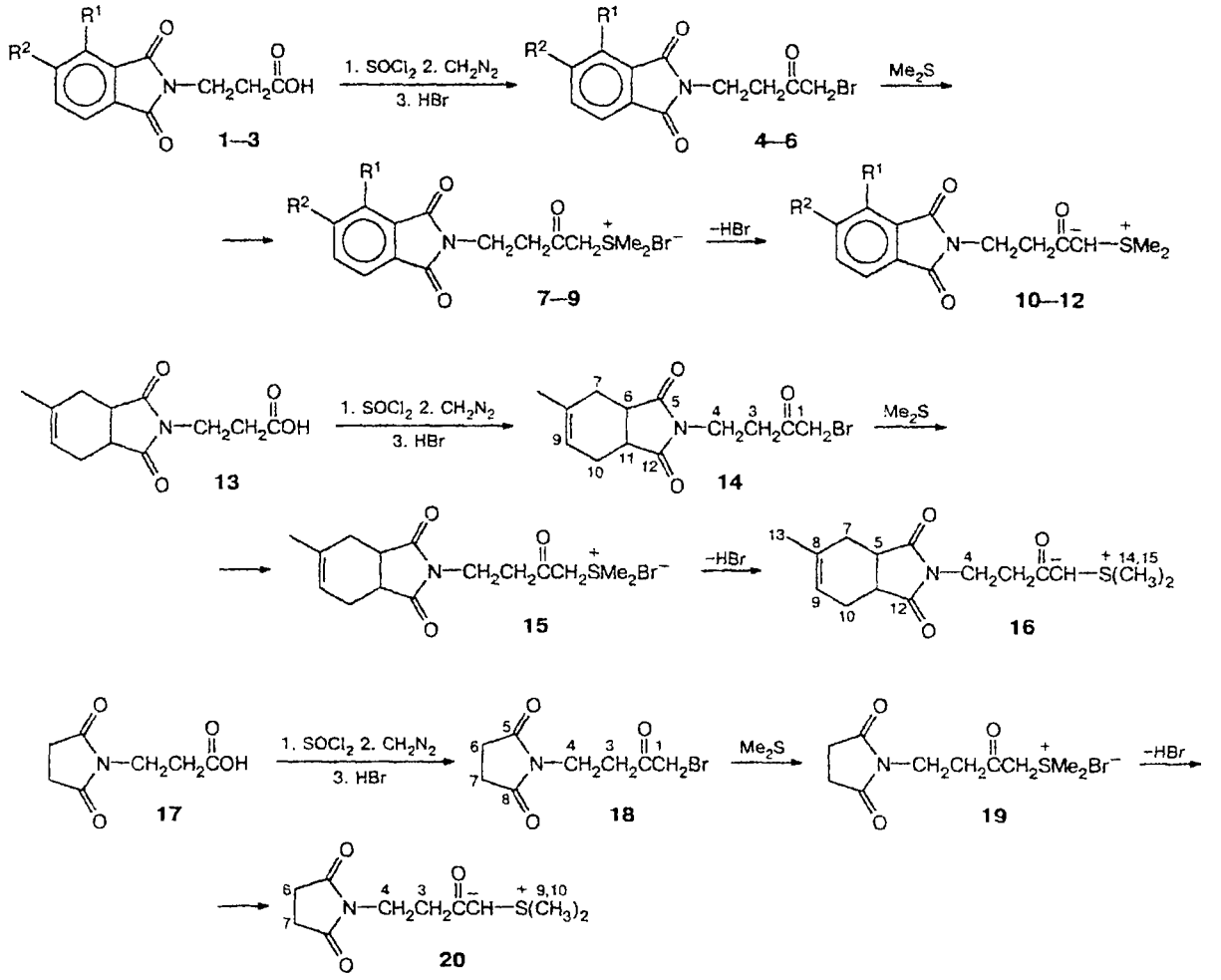
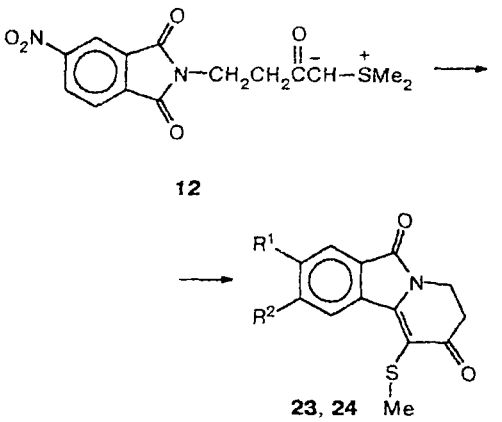
Scheme 1



$R^1 = NO_2$, $R^2 = H$ (**1**, **4**, **7**, **10**); $R^1 = Cl$, $R^2 = H$ (**2**, **5**, **8**, **11**); $R^1 = H$, $R^2 = NO_2$ (**3**, **6**, **9**, **12**)

the proton at the C(10) atom provides most information, because its interaction with the bulky sulfur atom should result in a downfield shift of this signal to 9 ppm, and this is actually observed for compounds **21** and **22**; the ^1H NMR spectra of these compounds exhibit signals at 9.01 and 9.35 ppm corresponding to one proton. These regularities can also be extended to the ^1H NMR spectra of compounds **23** and **24**. In fact, whereas in the spectrum of isomer **23**, the proton at C(10) is responsible for a signal at δ 9.17, in the case of isomer **24**, this signal is shifted to even a lower field, $\delta = 9.81$.

Unlike ylides **10**—**12**, sulfonium ylides **16** and **20**, containing 4-methyl-1,2,3,6-tetrahydrophthalimide and pyrrolidine-2,5-dione groups, respectively, do not form products of intramolecular cyclization under similar conditions. For example, thermolysis of ylide **16** affords mostly ketosulfide **25** and benzoate **26**, and ylide **20** is converted under the same conditions into a complex mixture of products.



12

23, **24**

$R^1 = NO_2$, $R^2 = H$ (**23**);
$R^1 = H$, $R^2 = NO_2$ (**24**)

Table 1. ^{13}C NMR spectra of α-bromomethyl ketones **4—6, 14, 18** and sulfonium ylides **10—12, 16, 20** (δ, $CDCl_3$, with respect to tetramethylsilane)

Atom	4	5	6	14	18	10	11	12	16	20
C(1)	33.75	33.36	33.29	33.94	33.81	51.30	52.03	51.24	51.44	51.90
C(2)	199.35	199.55	199.61	199.15	199.48	187.00	186.00	186.72	186.76	186.64
C(3)	33.94	33.80	36.75	33.94	34.20	37.01	36.09	36.95	36.82	36.82
C(4)	37.47	37.80	37.27	37.14	37.01	38.91	38.72	38.77	38.51	38.18
C(5)	162.67	165.67	166.06	179.64	176.96	169.00	165.34	166.00	179.77	177.09
C(6)	123.57	131.47	133.10	38.97	28.13	125.80	130.55	133.89	38.30	28.14
C(7)	144.98	127.61	117.82	28.39	28.13	144.90	127.42	118.48	28.29	28.14
C(8)	127.16	135.12	151.37	136.60	176.96	126.76	134.47	151.57	136.10	177.09
C(9)	135.58	135.84	129.64	119.98	—	134.92	135.12	128.92	120.04	28.46
C(10)	128.66	121.87	124.55	24.05	—	128.14	121.28	124.16	24.09	28.46
C(11)	133.88	134.01	136.36	39.43	—	134.40	133.95	136.75	39.30	—
C(12)	165.41	166.46	165.80	179.90	176.96	173.00	166.20	165.80	179.97	—
C(13)	—	—	—	23.43	—	28.13	28.20	28.20	28.46	—
C(14)	—	—	—	—	—	28.13	28.20	28.20	28.46	—
C(15)	—	—	—	—	—	—	—	—	23.43	—

Experimental

IR spectra were recorded on a Specord-M80 instrument. ^1H NMR spectra were obtained on Tesla BS-480 B and Bruker-AM 300 spectrometers operating at 100 and 300 MHz, respectively. ^{13}C NMR spectra were run on Jeol FX-90Q and Bruker-AM 300 instruments operating at 22.5 and 75 MHz, respectively, using tetramethylsilane as the internal standard.

Synthesis of *N*-acylated amino acids[7] 1—3, 13, 17 (general procedure). A mixture of β-alanine (0.06 mol) and thoroughly powdered cyclic anhydride (0.06 mol) was heated for 30 min on an oil bath at a temperature of 145—150 °C. After cooling, the solid product of the reaction was dissolved in 40 mL of methanol, the solution was filtered and diluted with 40 mL of water, and the precipitate was filtered off and dried.

3-(3-Nitrophthalimido)propionic acid (1). Yield 85%, m.p. 146—148 °C. Found (%): C, 49.75; H, 2.98; N, 10.61. $C_{11}H_8N_2O_6$. Calculated (%): C, 50.01; H, 3.05; N, 10.60. IR, ν/cm^{-1}: 1360, 1548, 1700, 1724, 1780, 2500—3500. ^1H NMR (acetone-d_6), δ: 2.7 (t, 2 H, CH_2, J = 7.0 Hz); 3.92 (t, 2 H, CH_2, J = 7.0 Hz); 8.17 (m, 3 H, C_6H_3); 9.3 (s, 1 H, COOH).

3-(3-Chlorophthalimido)propinoic acid (2). Yield 83%, m.p. 153—155 °C. Found (%): C, 51.85; H, 3.12; Cl, 14.19; N, 5.53. $C_{11}H_8NClO_4$. Calculated (%): C, 52.09; H, 3.18; Cl, 13.98; N, 5.52. IR, ν/cm^{-1}: 1700, 1775; 2500—3500. ^1H NMR (DMSO-d_6), δ: 2.62 (t, CH_2, J = 7.3 Hz); 3.72 (t, CH_2, J = 7.3 Hz); 7.82 (m, 3 H, C_6H_3).

3-(4-Nitrophthalimido)propionic acid (3). Yield 86%, m.p. 206—208 °C. Found (%): C, 49.80; H, 3.05; N, 10.6. $C_{11}H_8N_2O_6$. Calculated (%): C, 50.01; H, 3.05; N, 10.60. IR, ν/cm^{-1}: 1360, 1545, 1710, 1775, 2500—3500. ^1H NMR (acetone-d_6), δ: 2.65 (t, 2 H, CH_2, J = 7.0 Hz); 3.86 (t, 2 H, CH_2, J = 7.0 Hz); 7.73 (m, 3 H, C_6H_3).

3-(4-Methyl-1,2,3,6-tetrahydrophthalimido)propionic acid (13). Yield 79%, m.p. 95—97 °C. Found (%): C, 61.40; H, 5.60; N, 5.77. $C_{12}H_{13}NO_4$. Calculated (%): C, 61.27; H, 5.57; N, 5.95. IR, ν/cm^{-1}: 1690, 1713, 1775, 2500—3500. ^1H NMR (DMSO-d_6), δ: 1.64 (s, 3 H, CH_3); 2.23 (m, 4 H, 2 CH_2); 2.39 (t, 2 H, CH_2, J = 7.0 Hz); 3.16 (m, 2 H, CH); 3.55 (t, 2 H, CH_2, J = 7.0 Hz); 5.52 (s, 1 H, CH).

3-Succinimidopropionic acid (17). Yield 75%, m.p. 133—134 °C. Found (%): C, 48.96; H, 5.28; N, 8.20. $C_7H_9NO_4$. Calculated (%): C, 49.12; H, 5.30; N, 8.18. IR, ν/cm^{-1}: 1680, 1725, 1770, 2500—3500. ^1H NMR (D_2O), δ: 2.63 (t, 2 H, CH_2, J = 7.0 Hz); 2.78 (s, 4 H, CH_2—CH_2); 3.75 (t, 2 H, CH_2, J = 7.0 Hz).

Synthesis of bromo ketones 4—6, 14, and 18 (general procedure). An ethereal solution of diazomethane prepared from 0.4 mol of nitrosomethylurea was placed in a three-necked flask equipped with a stirrer, a dropping funnel, and a thermometer. At 0 °C, a solution of protected β-alanine chloride (0.1 mol) in 100 mL of ether was added dropwise with stirring. When the evolution of nitrogen ceased, the reaction mixture was stirred for an additional 1 h. To the resulting solution (or suspension) of the diazoketone, 100 mL of concentrated HBr was added dropwise with stirring. When the addition was completed, the reaction mixture was heated at reflux for 1 h, cooled, and diluted with three volumes of water. The ethereal layer was separated, washed with an aqueous solution of $NaHCO_3$, and dried with $MgSO_4$. The solvent was evaporated, and the resulting bromo ketone was recrystallized.

1-Bromo-4-(3-nitrophthalimido)butan-2-one (4). Yield 75%, m.p. 104—105 °C. Found (%): C, 41.98; H, 2.71; Br, 22.75; N, 8.19. $C_{12}H_9BrN_2O_5$. Calculated (%): C, 42.25; H, 2.66; Br, 23.42; N, 8.21. IR, ν/cm^{-1}: 1368, 1540, 1716, 1776. ^1H NMR ($CDCl_3$), δ: 3.15 (t, 2 H, CH_2, J = 7.0 Hz); 3.93 (t, 2 H, CH_2Br); 4.04 (t, 2 H, CH_2, J = 7.0 Hz); 7.84—8.18 (m, 3 H, C_6H_3).

1-Bromo-4-(3-chlorophthalimido)butan-2-one (5). Yield 70%, m.p. 120—122 °C. Found (%): C, 43.62; H, 2.61; Cl, 9.98; Br, 24.08; N, 4.25. $C_{12}H_9BrClNO_3$. Calculated (%): C, 43.60; H, 2.74; Cl, 10.74; Br, 24.17; N, 4.24. IR, ν/cm^{-1}: 1695, 1730, 1770. ^1H NMR ($CDCl_3$), δ: 3.13 (t, 2 H, CH_2, J = 7.0 Hz); 3.96 (s, 2 H, CH_2Br); 4.00 (t, 2 H, CH_2, J = 7.0 Hz); 7.62—7.78 (m, 3 H, C_6H_3).

1-Bromo-4-(4-nitrophthalimido)butan-2-one (6). Yield 71%, m.p. 206—208 °C. Found (%): C, 41.83; H, 2.60; Br, 2.60; N, 8.17. $C_{12}H_9BrN_2O_5$. Calculated (%): C, 42.25; H, 2.66; Br, 23.42; N, 8.21. IR, ν/cm^{-1}: 1360, 1540, 1717, 1735, 1775. ^1H NMR ($CDCl_3$), δ: 3.16 (t, 2 H, CH_2CO, J = 7.0 Hz); 3.92 (s, 2 H, CH_2Br); 4.07 (t, 2 H, CH_2, J = 7.0 Hz); 8.00—8.66 (m, 2 H, C_6H_3); 8.66 (s, 1 H, C_6H_3).

1-Bromo-4-(4-methyl-1,2,3,6-tetrahydrophthalimido)butan-2-one (14). Yield 58%, m.p. 78—79 °C. Found (%): C, 49.85; H, 4.38; Br, 24.15; N, 4.50. $C_{13}H_{14}BrNO_3$. Calculated (%): C, 50.02; H, 4.52; Br, 25.60; N, 4.48. IR, ν/cm^{-1}: 1692, 1728,

1768. ^{1}H NMR ($CDCl_3$), δ: 1.72 (s, 3 H, CH_3); 2.3 (m, 4 H, CH_2); 2.99 (t, 2 H, CH_2CO, J = 7.0 Hz); 3.31 (m, 2 H, CH); 3.76 (t, 2 H, CH_2, J = 7.0 Hz); 3.92 (s, 2 H, CH_2Br); 5.52 (br.s, 1 H, CH).

1-Bromo-4-succinimidobutan-2-one (18). Yield 62%, m.p. 73—74 °C. Found (%): C, 38.84; H, 4.03; Br, 31.86; N, 5.55. $C_8H_{10}BrNO_3$. Calculated (%): C, 38.83; H, 4.06; Br, 32.21; N, 5.65. IR, ν/cm^{-1}: 1700, 1775. ^{1}H NMR ($CDCl_3$), δ: 2.72 (s, 4 H, CH_2CH_2); 3.00 (t, 2 H, CH_2CO, J = 7.0 Hz); 3.82 (t, 2 H, CH_2, J = 7.0 Hz); 3.93 (s, 2 H, CH_2Br).

Synthesis of sulfonium salts 7—9, 15, 19 (general procedure). Dimethyl sulfide (30 mmol) was added with stirring to a solution of bromo ketone (10 mmol) in 50 mL of acetone, and the reaction mixture was kept at ~20 °C for 10—14 h. The precipitate was filtered off and washed with acetone.

4-(3-Nitrophthalimido)-2-oxobutane-1-dimethylsulfonium bromide (7). Yield 76%, m.p. 103—105 °C. Found (%): C, 41.70; H, 3.76; Br, 19.27; N, 6.78; S, 7.18. $C_{14}H_{15}BrN_2O_5S$. Calculated (%): C, 41.65; H, 3.75; Br, 19.81; N, 6.95; S, 7.95. IR, ν/cm^{-1}: 1360, 1536, 1712, 1776. ^{1}H NMR (CF_3COOH), δ: 2.8 (s, 6 H, SMe_2); 2.96 (t, 2 H, CH_2CO, J = 7.0 Hz); 3.86 (t, 2 H, CH_2, J = 7.0 Hz); 4.57 (s, 2 H, CH_2); 7.86 (m, 3 H, C_6H_3).

4-(3-Chlorophthalimido)-2-oxobutane-1-dimethylsulfonium bromide (8). Yield 73%, m.p. 91—93 °C. Found (%): C, 42.80; H, 3.46; Br, 19.58; Cl, 8.70; N, 3.40; S, 7.66. $C_{14}H_{15}BrClNO_3S$. Calculated (%): C, 42.82; H, 3.85; Br, 20.35; Cl, 9.03; N, 3.75; S, 8.16. IR, ν/cm^{-1}: 1712, 1776. ^{1}H NMR (CF_3COOH), δ: 2.66 (s, 6 H, SMe_2); 2.87 (t, 2 H, CH_2CO, J = 7.0 Hz); 3.73 (t, 2 H, CH_2, J = 7.0 Hz); 4.48 (s, 2 H, CH_2S); 7.33 (s, 3 H, C_6H_3).

4-(4-Nitrophthalimido)-2-oxobutane-1-dimethylsulfonium bromide (9). Yield 85%, m.p. 135—137 °C. Found (%): C, 41.18; H, 3.24; Br, 19.18; N, 6.70; S, 7.80. $C_{14}H_{15}BrN_2O_5S$. Calculated (%): C, 41.70; H, 3.75; Br, 19.81; N, 6.95; S, 7.95. IR, ν/cm^{-1}: 1358, 1555, 1718, 1776. ^{1}H NMR (CF_3COOH), δ: 2.68 (s, 6 H, SMe_2); 2.88 (t, 2 H, CH_2CO, J = 7.0 Hz); 3.78 (t, 2 H, CH_2, J = 7.0 Hz); 4.47 (s, 2 H, CH_2S); 7.67—8.32 (m, 3 H, C_6H_3).

4-(4-Methyl-1,2,3,6-tetrahydrophthalimido)-2-oxobutane-1-dimethylsulfonium bromide (15). Yield 73%, m.p. 78—79 °C. Found (%): C, 48.28; H, 5.20; Br, 20.91; N, 3.91; S, 8.26. $C_{15}H_{20}BrNO_3S$. Calculated (%): C, 48.13; H, 5.29; Br, 21.35; N, 3.74; S, 8.57. IR, ν/cm^{-1}: 1700, 1770.

4-Succinimido-2-oxobutane-1-dimethylsulfonium bromide (19). Yield 78%, m.p. 111—112 °C. Found (%): C, 38.61; H, 3.28; Br, 24.60; N, 4.40; S, 9.88. $C_{10}H_{10}BrNO_3S$. Calculated (%): C, 38.71; H, 5.20; Br, 25.78; N, 4.52; S, 10.34. IR, ν/cm^{-1}: 1690, 1712, 1768. ^{1}H NMR (CF_3COOH), δ: 2.60 (s, 4 H, $(CH_2CO)_2$); 2.83 (t, 2 H, CH_2CO, J = 7.0 Hz); 2.85 (s, 6 H, SMe_2); 3.65 (t, 2 H, CH_2, J = 7.0 Hz); 4.6 (s, 2 H, CH_2S).

Synthesis of sulfonium ylides 10—12, 16, 20 (general procedure). A 12.5 N solution of NaOH (0.7 mL) and a saturated solution of K_2CO_3 (4 mL) were added with stirring to a suspension of sulfonium salt (5.6 mmol) in 10 mL of $CHCl_3$ cooled to 10 °C. The reaction mixture was stirred for 15 min and warmed to ~20 °C, the precipitated inorganic salt was filtered off, and the organic layer was dried with K_2CO_3. Evaporation of the solvent gave sulfonium ylide.

1-Dimethylsulfuranylidene-4-(3-nitrophthalimido)butan-2-one (10). Yield 12%. Found (%): C, 52.05; H, 4.17; N, 8.60; S, 8.89. $C_{14}H_{14}N_2O_5S$. Calculated (%): C, 52.17; H, 4.38; N, 8.69; S, 9.95. IR, ν/cm^{-1}: 1545, 1720, 1776. ^{1}H NMR ($CDCl_3$), δ: 2.47 (t, 2 H, CH_2CO, J = 7.0 Hz); 2.87 (s, 6 H, SMe_2); 3.65 (s, 1 H, CH); 4.01 (t, 2 H, CH_2, J = 7.0 Hz); 7.78—8.16 (m, 3 H, C_6H_3).

1-Dimethylsulfuranylidene-4-(3-chlorophthalimido)butan-2-one (11). Yield 95%. Found (%): C, 54.00; H, 4.56; Cl, 10.84; N, 4.39; S, 10.16. $C_{14}H_{14}ClNO_3S$. Calculated (%): C, 53.93; H, 4.53; Cl, 11.37; N, 4.49; S, 10.28. IR, ν/cm^{-1}: 1555, 1710, 1776. ^{1}H NMR ($CDCl_3$), δ: 2.46 (t, 2 H, CH_2CO, J = 7.0 Hz); 2.86 (s, 6 H, SMe_2); 3.58 (s, 1 H, CH); 3.71 (t, 2 H, CH_2, J = 7.0 Hz); 7.60—7.80 (m, 3 H, C_6H_3).

1-Dimethylsulfuranylidene-4-(4-nitrophthalimido)butan-2-one (12). Yield 62%. Found (%): C, 52.01; H, 4.20; N, 8.71; S, 9.10. $C_{14}H_{14}N_2O_5S$. Calculated (%): C, 52.17; H, 4.38; N, 8.69; S, 9.95. IR, ν/cm^{-1}: 1550, 1720, 1776. ^{1}H NMR ($CDCl_3$), δ: 2.48 (t, 2 H, CH_2CO, J = 7.0 Hz); 2.85 (s, 6 H, SMe_2); 3.62 (s, 1 H, CH); 4.02 (t, 2 H, CH_2, J = 7.0 Hz); 8.62 (s, 1 H, C_6H_3); 8.55—7.79 (m, 2 H, C_6H_3).

1-Dimethylsulfuranylidene-4-(4-methyl-1,2,3,6-tetrahydrophthalimido)butan-2-one (16). Yield 85%. Found (%): C, 61.20; H, 6.50; N, 4.70; S, 9.40. $C_{15}H_{19}NO_3S$. Calculated (%): C, 61.41; H, 6.53; N, 4.77; S, 10.93. Mol. weight 293.4. IR, ν/cm^{-1}: 1545, 1700, 1770. ^{1}H NMR ($CDCl_3$), δ: 1.70 (s, 3 H, CH_3); 2.28 (t, 2 H, CH_2CO, J = 7.0 Hz); 2.40 (m, 4 H, 2 CH_2); 2.87 (s, 6 H, SMe_2); 3.40 (m, 2 H, CH); 3.60 (s, 1 H, CH); 3.71 (t, 2 H, CH_2, J = 7.0 Hz); 5.52 (m, CH).

1-Dimethylsulfuranylidene-4-succinimidobutan-2-one (20). Yield 55%. Found (%): C, 52.10; H, 6.50; N, 6.09; S, 12.90. $C_{10}H_{15}NO_3S$. Calculated (%): C, 52.38; H, 6.59; N, 6.11; S, 13.98. Mol. weight 229.3. IR, ν/cm^{-1}: 1445, 1700, 1770. ^{1}H NMR ($CDCl_3$), δ: 2.35 (t, 2 H, CH_2CO, J = 6.8 Hz); 2.68 (s, 4 H, succinimide); 2.87 (s, 6 H, SMe_2); 3.60 (s, 1 H, CH); 3.77 (t, 2 H, CH_2, J = 7.0 Hz).

Intramolecular cyclization of sulfonium ylides 10—12, 16, 20 (general procedure).[6] Sulfonium ylide (2 mmol) was dissolved with heating in 8 mL of dry toluene, and benzoic acid (2 mmol) was added. The mixture was refluxed for 1.5 h. The toluene was evaporated, and the product was isolated by column chromatography on SiO_2 (ethyl acetate : hexane, 1 : 1).

1-Methylthio-7-nitro-3,4-dihydropyrido[2,1-*a*]isoindole-2,6-dione (21). Yield 52%. Found (%): C, 53.40; H, 3.30; N, 9.95; S, 10.87. $C_{13}H_{10}N_2O_4S$. Calculated (%): C, 53.79; H, 3.47; N, 9.65; S, 11.05. IR, ν/cm^{-1}: 1364, 1536, 1664, 1720, 1776. ^{1}H NMR ($CDCl_3$), δ: 2.43 (s, 3 H, CH_3S); 2.89 (t, 2 H, CH_2CO, J = 7.5 Hz); 4.17 (t, 2 H, CH_2, J = 7.04 Hz); 7.92—9.35 (m, 3 H, C_6H_3).

7-Chloro-1-methylthio-3,4-dihydropyrido[2,1-*a*]isoindole-2,6-dione (22). Yield 75%, m.p. 209 °C. Found (%): C, 59.40; H, 3.49; Cl, 12.43; N, 5.08; S, 10.86. $C_{13}H_{10}ClNO_2S$. Calculated (%): C, 55.82; H, 3.60; Cl, 12.67; N, 5.01; S, 11.46. IR, ν/cm^{-1}: 1580, 1670, 1720, 1778. ^{1}H NMR ($CDCl_3$), δ: 2.39 (s, 3 H, CH_3S); 2.89 (t, 2 H, CH_2CO, J = 7.02 Hz); 4.13 (t, 2 H, CH_2, J = 7.22 Hz); 7.57—9.01 (m, 3 H, C_6H_3).

1-Methylthio-8-nitro-3,4-dihydropyrido[2,1-*a*]isoindole-2,6-dione (23). Yield 38%, m.p. 180—182 °C. Found (%): C, 53.68; H, 3.27; N, 9.71; S, 10.18. $C_{13}H_{10}N_2O_4S$. Calculated (%): C, 53.79; H, 3.47; N, 9.65; S, 11.05. Mol. weight 290.3. IR, ν/cm^{-1}: 1356, 1528, 1576 1664, 1724. ^{1}H NMR ($CDCl_3$), δ: 2.46 (s, 3 H, CH_3S); 2.91 (t, 2 H, CH_2CO, J = 7.2 Hz); 8.56 (s, 1 H, C_6H_3, J = 8.7 Hz); 8.70 (s, 1 H, C_6H_3); 9.17 (d, 1 H, C_6H_5, J = 8.7 Hz).

1-Methylthio-9-nitro-3,4-dihydropyrido[2,1-*a*]isoindole-2,6-dione (24). Yield 35%, m.p. 200—202 °C. Found (%): C, 53.60; H, 3.40; N, 9.68; S, 10.75. $C_{13}H_{10}N_2O_4S$. Calculated (%): C, 53.79; H, 3.47; N, 9.65; S, 11.05. Mol. weight 290.3. IR, ν/cm^{-1}: 1355, 1530, 1576, 1665, 1725. ^{1}H NMR ($CDCl_3$), δ: 2.48 (s, 3 H, CH_3S); 2.91 (t, 2 H, CH_2CO, J = 7.2 Hz); 4.21 (t, 2 H, CH_2, J = 7.2 Hz); 8.04—8.67 (m, 2 H, C_6H_3); 9.81 (d, 1 H, C_6H_3, J = 8.7 Hz).

Synthesis of compounds 25 and 26. A mixture of compounds **25** and **26** was prepared from ylide **16** under similar conditions.

1-Methylthio-4-(4-methyl-1,2,3,6-tetrahydrophthalimido)-butan-2-one (25) was isolated by column chromatography in a yield of 37%. Found (%): C, 59.13; H, 6.19; N, 4.73; S, 10.06. $C_{14}H_{19}NO_3S$. Calculated (%): C, 59.76; H, 6.81; N, 4.98; S, 11.40. Mol. weight 281.4. IR, ν/cm^{-1}: 1600, 1692, 1720, 1768. ^{13}C NMR ($CDCl_3$), δ: 15.66 (q, CH_3S); 23.41 (q, CH_3); 24.16 (t); 28.61 (t); 34.08 (t); 37.80 (t); 42.80 (t, CH_2); 39.01 (d); 39.44 (d, CH); 120.06 (d, CH=C); 136.31 (s, C=CH); 179.72 (s, CON); 202.93 (s, CO).

1-Benzoyloxy-4-(4-methyl-1,2,3,6-tetrahydrophthalimido)-butan-2-one (26) was isolated by column chromatography in a yield of 34%. Found (%): C, 67.01; H, 5.24; N, 3.80. $C_{20}H_{21}NO_5$. Calculated (%): C, 67.59; H, 5.96; N, 3.94. IR, ν/cm^{-1}: 1602, 1700, 1720, 1776. ^{13}C NMR ($CDCl_3$), δ: 23.29 (q, CH_3); 24.06 (t); 28.55 (t); 33.32 (t); 36.25 (t); 68.11 (t, CH_2); 38.96 (d); 39.39 (d, CH); 165.58 (s, CO_2); 179.60 (s); 179.88 (s, CON); 201.74 (s, CO); 128.95 (s); 128.41 (d); 129.76 (d); 133.39 (d, C_6H_5).

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