Sulfur ylides
13.* Synthesis and intramolecular cyclization of keto-stabilized sulfur ylides

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Keto-stabilized sulfur mono- and bisylides were obtained from *N*-phthalylglutamic acid and their intramolecular cyclization was studied. The intramolecular cyclization of the ylide obtained at the α-carboxy group gave a product of the pyrrolizidinedione structure; bisylide yielded a cycloheptene derivative as the result of intramolecular recombination of intermediate dicarbene. The ylide obtained at the γ-carboxy group underwent no cyclization, giving methylthio ketone and oxo benzoate.

Key words: *N*-phthalylglutamic acid, keto-stabilized sulfonium ylide, intramolecular cyclization, intramolecular recombination of dicarbene.

To proceed further in our investigations concerning the synthesis of keto-stabilized sulfonium ylides from α- and β-amino acids and their intramolecular cyclization,[1—8] we obtained novel sulfur ylides from *N*-phthalylglutamic acid. Dibasic glutamic acid can form three sulfur ylides involving either the α- or γ-carboxyl groups or both (they are conventionally denoted as α-ylide, γ-ylide, and bisylide, respectively).

As shown earlier,[5,8] sulfonium ylides can be obtained from amino acids in two ways: by the salt method (deprotonation of a sulfonium salt prepared from the corresponding diazo ketone[8]) or by the carbene method (reaction of Me_2S with a carbene generated from diazo ketone in the presence of a catalyst[5]). In the latter case, the ylide is involved in *in situ* intramolecular cyclization. To compare both the methods in efficiency, we synthesized ylides in either way.

In Schemes 1—3, the syntheses of γ-ylide **6**, bisylide **13**, and α-ylide **19** are shown, respectively.

γ-Ylide **6** was obtained from diazo ketone **3** prepared by the Arndt—Eistert reaction of *N*-phthalylglutamic acid (**1**) with $SOCl_2$ to predominantly form anhydride **2**, which was then treated with a solution of diazomethane in CH_2Cl_2.

For the synthesis of bisylide **13**, *N*-phthalylglutamic acid **1** was converted into dichloride **9** with PCl_5 and then into bis(diazo ketone) **10** in 98% yield.

For the synthesis of α-ylide **19**, α-diazo ketone **16** was obtained from γ-methyl *N*-phthalylglutamate **15** by the Arndt—Eistert reaction.

The structures of diazo ketones **3**, **10**, and **16** were confirmed by spectroscopic data. Their IR spectra contain intense absorption bands of the diazo group at ν = 2116 (**3**) and 2110 cm^{-1} (**10**, **16**). In the ^{13}C NMR spectra, signals for the C atoms of the CHN_2 group appear at δ_C 54.75 (**3**), 54.94, 54.3 (**10**), and 54.6 (**16**). The ^1H NMR spectra show a singlet for the CHN_2 proton at δ_H 5.22 (**3**), 5.22, 5.48 (**10**), and 5.48 (**16**).

Subsequently, ylides **6**, **13**, and **19** were synthesized according to a general procedure.

In the case of the salt method, diazo ketones **3**, **10**, and **16** were treated with aqueous HBr to give α-bromomethyl ketones **4**, **11**, and **17**, whose reactions with Me_2S yielded sulfonium salts **5**, **12**, and **18**. Their deprotonation with NaH in THF under argon gave keto-stabilized sulfur ylides **6**, **13**, and **19**, respectively.

The structures of all the compounds obtained were confirmed by spectroscopic data. In the ^{13}C NMR spectra of bromo ketones **4**, **11**, and **17**, signals for the methylene C atom of the CH_2Br group at δ_C 36.07 (**4**), 30.56, 36.45 (**11**), and 30.93 (**17**) are informative. The ^1H NMR spectra of sulfonium salts **5**, **12**, and **18** show singlets for the methyl protons of the SMe_2 group at δ_H 2.8.

It is worth noting that all the ylides obtained are unstable and rapidly decompose into several products even at room temperature, which makes it difficult to record the spectra of individual ylides. Yet they can be detected from a longer-wavelength shift (characteristic of keto-stabilized ylides) of the absorption band of the CO group bound to the carbanion to ν = 1540 cm^{-1} in the IR spectra and from an upfield shift of the signal for the C atom of this group to δ 182 in the ^{13}C NMR spectra, which sug-

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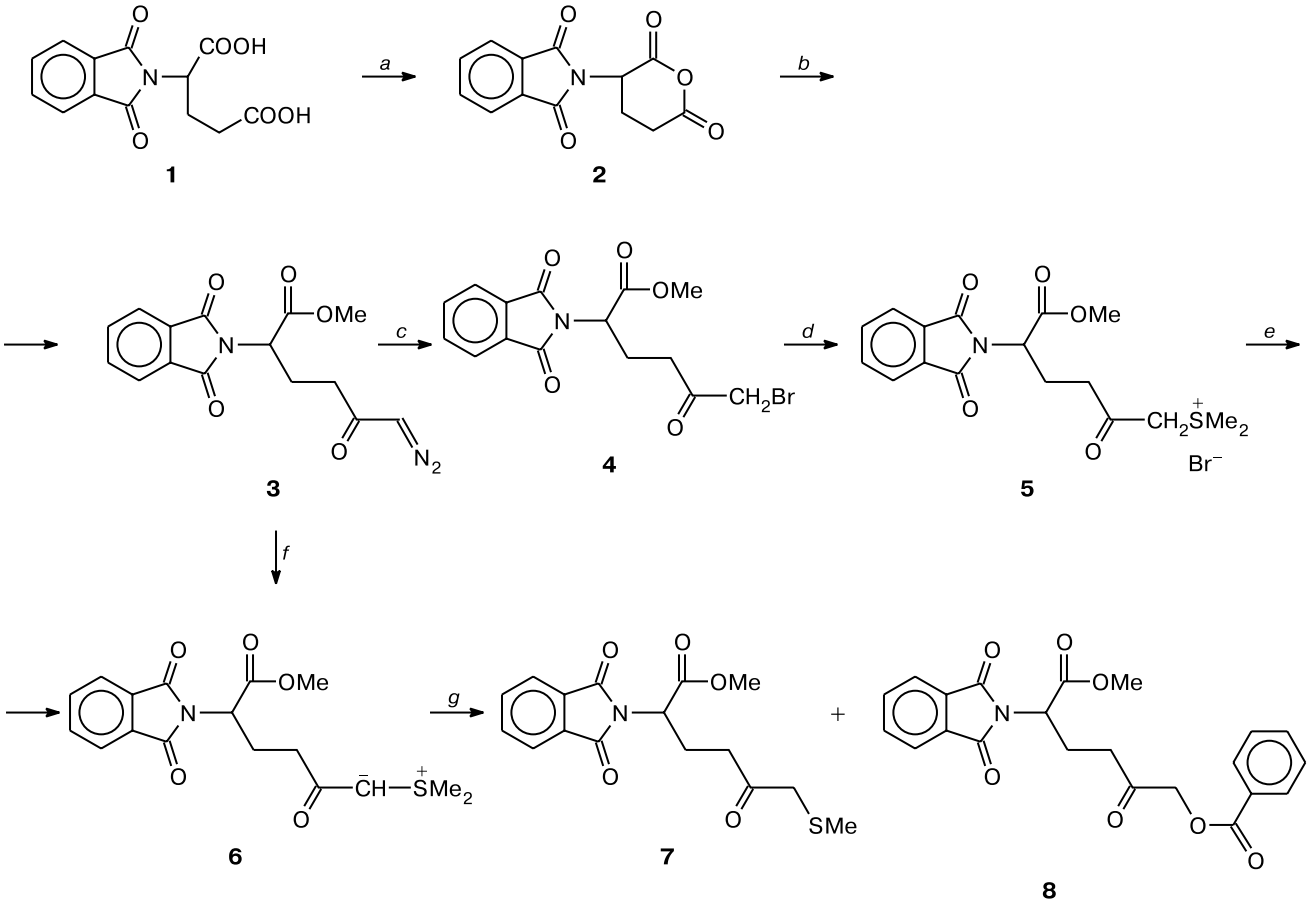
Scheme 1



Reagents and conditions: *a*. $SOCl_2$, PhH, 80 °C; *b*. CH_2N_2, CH_2Cl_2, −5 °C; *c*. HBr, CH_2Cl_2, ~20 °C; *d*. Me_2S, Me_2CO, ~20 °C; *e*. NaH, THF, ~20 °C; *f*. $Rh_2(OAc)_4$, Me_2S, PhH, 80 °C; *g*. BzOH, PhMe, 110 °C.

gests delocalization of the negative charge on the carbonyl group. The formation of ylides was also confirmed by elemental analysis data immediately upon their syntheses.

In the case of the carbene method, ylide were obtained by decomposition of diazo ketones **3**, **10**, and **16** in the presence of Me_2S and the catalyst $Rh_2(OAc)_4$ in boiling benzene. Benzene was used as a solvent because of the high stabilities of diazo ketones, which keep inert at lower temperatures. The course of the reactions and the formation of ylides was monitored by TLC. After removal of the solvent and addition of toluene and BzOH, we attempted intramolecular cyclization of ylides **6**, **13**, and **19**.

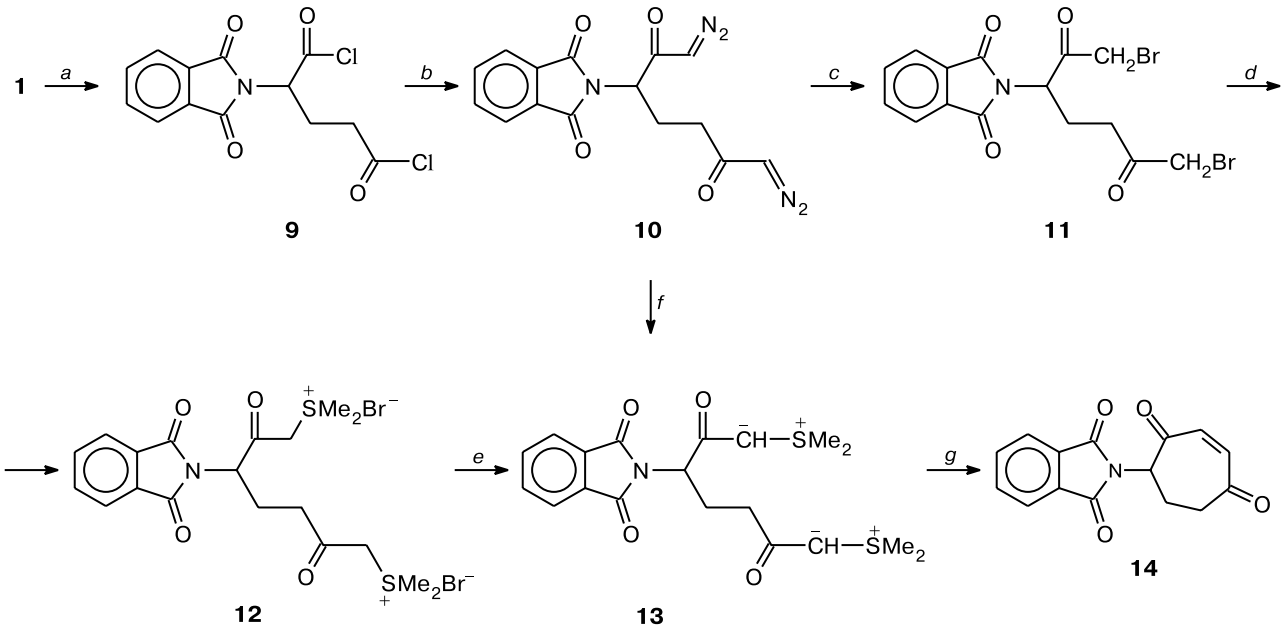
The study of the behavior of the ylides under the conditions of intramolecular cyclization (boiling toluene, an equimolar amount of BzOH as a catalyst)[7] revealed that sulfur γ-ylide **6** yields acyclic sulfide **7** (19%) and oxo benzoate **8** (32%). Ylide **6** obtained according to the carbene method under the same conditions forms a difficult-to-separate mixture of products. However, in the absence of benzoic acid, the reaction gives sulfide **7** in 35% yield (with respect to diazo ketone).

Under the conditions of intramolecular cyclization, bisylide **13** converted into cycloheptene derivative **14**, which can be explained by the generation of an intermediate dicarbene from bisylide **13**.[9] The yield of product **14** was 40% (with respect to ylide **13**) or 12% (with respect to diazo ketone **10**) for the salt method and 17% for the carbene method.

α-Ylide **19** underwent spontaneous cyclization even at room temperature to give pyrrolizidinedione **20**. In boiling toluene in the presence of BzOH, its yield was 56% (with respect to ylide **19**) or 31% (with respect to diazo ketone **16**). Under the same conditions, ylide **19** obtained according to the carbene method underwent intramolecular cyclization to give product **20** in 10% yield.

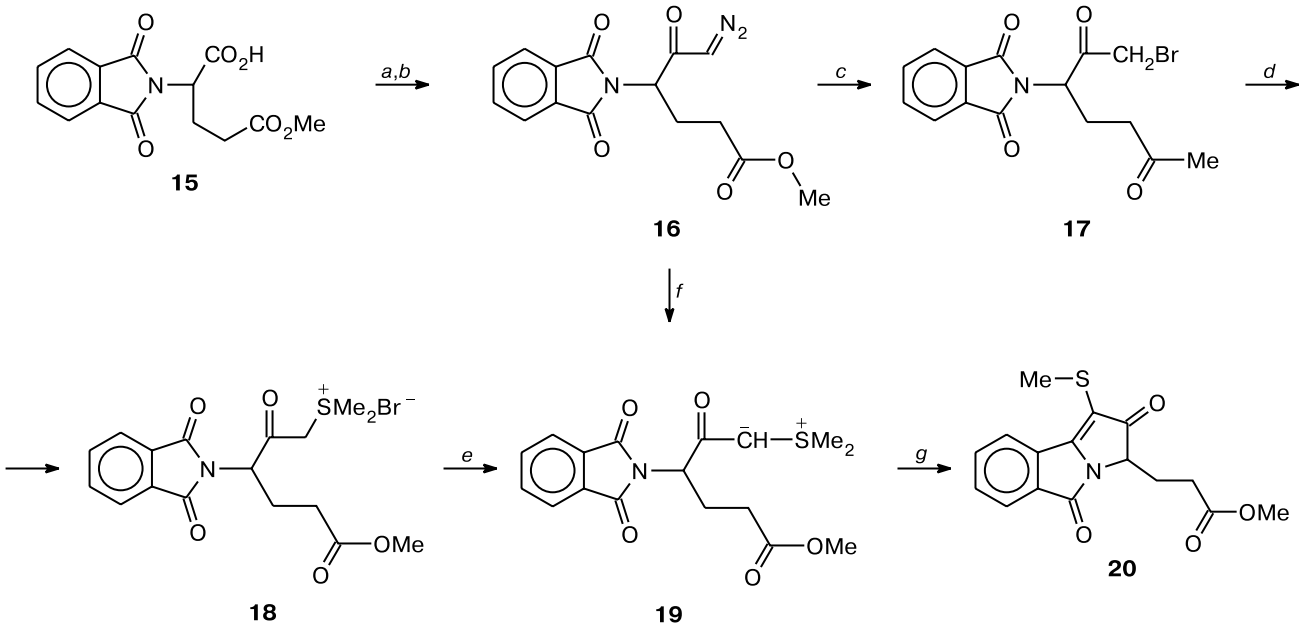
Thus, we obtained novel keto-stabilized sulfonium ylides from *N*-phthalylglutamic acid. It was found that only α-ylide **19** undergoes intramolecular cyclization into a pyrrolizidinedione structure, while for ylides **6** and **13**,

Scheme 2



Reagents and conditions: *a*. PCl_5, CCl_4, 77 °C; *b*. CH_2N_2, CH_2Cl_2, –5 °C; *c*. HBr, CH_2Cl_2, ~20 °C; *d*. Me_2S, Me_2CO, ~20 °C; *e*. NaH, THF, ~20 °C; *f*. $Rh_2(OAc)_4$, Me_2S, PhH, 80 °C; *g*. BzOH, PhMe, 110 °C.

Scheme 3



Reagents and conditions: *a*. $SOCl_2$, PhH, 80 °C; *b*. CH_2N_2, CH_2Cl_2, –5 °C; *c*. HBr, CH_2Cl_2, ~20 °C; *d*. Me_2S, Me_2CO, ~20 °C; *e*. NaH, THF, ~20 °C; *f*. $Rh_2(OAc)_4$, Me_2S, PhH, 80 °C; *g*. BzOH, PhMe, 110 °C.

competitive reactions are thermodynamically more favorable: generation of an intermediate dicarbene followed by its intramolecular recombination for ylide **13** and the formation of methylthio ketone and oxo benzoate for ylide **6**. The relatively low yields of the compounds obtained are due to the instabilities of ylides, which decom-

pose under the reaction conditions to give many by-products that are difficult to separate.

Experimental

IR spectra were recorded on a UR-20 and Specord M-80 instruments (Nujol). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer (300 and 75 MHz, respectively) in $CDCl_3$ (except for salts **5**, **12**, and **18**) with Me_4Si as the internal standard. The course of the reactions was monitored by TLC on Silufol UV-254 plates; spots were visualized under UV light, in the iodine vapor, and with ninhydrin or with a solution of anisaldehyde followed by heating to 100—120 °C. Reaction products were isolated by column chromatography on silica gel with light petroleum—ethyl acetate (8 : 2) as an eluent. The solvents Me_2CO and CCl_4 were distilled over P_2O_5, toluene and benzene were refluxed and distilled over metallic sodium, $SOCl_2$ and CH_2Cl_2 were distilled, and Me_2S was dried over 4A molecular sieves. Phthalic anhydride (analytical grade), glutamic acid (high-purity grade), methyl glutamate (high-purity grade), PCl_5 (analytical grade), 48% HBr (analytical grade), NaH (60—65% dispersion in an oil; Fluka) were used as purchased.

2-(1,3-Dioxo-2,3-dihydro-1*H*-isoindol-2-yl)pentanedioic acid (1) and 2-(1,3-dioxo-2,3-dihydro-1*H*-isoindol-2-yl)-5-methoxy-5-oxopentanoic acid (15) were prepared according to a known procedure.[10]

Methyl 6-diazo-2-(1,3-dioxo-1,3-dihydro-1*H*-isoindol-2-yl)-5-oxohexanoate (3) and methyl 6-diazo-4-(1,3-dioxo-2,3-dihydro-1*H*-isoindol-2-yl)-5-oxohexanoate (16). Thionyl chloride (50 mmol) was added to a suspension of compound **1** or **15** (20 mmol) in dry benzene (100 mL) and the reaction mixture was refluxed until gas evolution ceased (~3 h). The solvent and the excess of $SOCl_2$ were removed and the resulting acid chloride was used without additional purification in a reaction with CH_2N_2. A solution of the acid chloride (10 mmol) in CH_2Cl_2 (20 mL) was added dropwise at −5 °C to a stirred solution of CH_2N_2 in CH_2Cl_2 prepared from nitrosomethylurea (NMU) (40 mmol). The solution was stirred at this temperature for 0.5 h and left in a refrigerator for 12 h. The solvent was removed and diazo ketones **3** and **16** were isolated by column chromatography.

The yield of compound **3** was 71%. Found (%): C, 57.03; H, 4.17; N, 13.25. $C_{15}H_{13}N_3O_5$. Calculated (%): C, 57.14; H, 4.16; N, 13.33. IR, ν/cm^{-1}: 1636, 1714, 1774, 1750, 2116. ^{1}H NMR, δ: 2.32—2.52, 2.52—2.69 (both m, 2 H each, CH_2); 3.71 (s, 3 H, Me); 4.85—4.93 (m, 1 H, CH); 5.22 (s, 1 H, CH); 7.69—7.90 (m, 4 H, C_6H_4). ^{13}C NMR, δ: 24.2, 30.5, 51.7, 52.8, 54.7, 123.6, 131.6, 134.3, 167.5, 169.2, 192.9.

The yield of compound **16** was 62%. Found (%): C, 56.8; H, 4.45; N, 13.64. $C_{15}H_{13}N_3O_5$. Calculated (%): C, 57.14; H, 4.16; N, 13.33. IR, ν/cm^{-1}: 1650, 1731, 1780, 2110. ^{1}H NMR, δ: 2.29—2.37, 2.44—2.54 (both m, 2 H each, CH_2); 3.55 (s, 3 H, Me); 4.78—4.87 (m, 1 H, CH); 5.48 (s, 1 H, CH); 7.69—7.88 (m, 4 H, C_6H_4). ^{13}C NMR, δ: 23.2, 30.4, 51.6, 54.6, 56.0, 123.5, 131.3, 134.3, 167.5, 172.5, 188.9.

1,7-Bisdiazo-3-(1,3-dioxo-2,3-dihydro-1*H*-isoindol-2-yl)-2,6-dioxoheptane (10). Phosphorus pentachloride (10 g, 50 mmol) was added to a suspension of acid **1** (5.54 g, 20 mmol) in dry CCl_4 (100 mL). The reaction mixture was refluxed until gas evolution ceased (~3 h) and cooled to room temperature. The precipitate of anhydride **2** (18%) that formed was filtered off. The solvent was removed to give acid dichloride **9** in 79% yield, which was employed without additional purification for the synthesis of bis(diazo ketone) **10** as described above. A solution of acid dichloride **9** (3 g, 10 mmol) in CH_2Cl_2 (20 mL) and a solution of diazomethane prepared from NMU (6.6 g, 80 mmol) were used.

The yield of compound **10** was 98%. Found (%): C, 55.31; H, 3.10; N, 21.87. $C_{15}H_{11}N_5O_4$. Calculated (%): C, 55.39; H, 3.41; N, 21.53. IR, ν/cm^{-1}: 1636, 1714, 1774, 2110. ^{1}H NMR, δ: 2.34—2.40, 2.50—2.58 (both m, 2 H each, CH_2); 4.79—4.85 (m, 1 H, CH); 5.22, 5.48 (both s, 1 H each, CH); 7.69—7.90 (m, 4 H, C_6H_4). ^{13}C NMR, δ: 23.4, 37.0, 54.3, 54.9, 56.5, 123.7, 131.5, 134.5, 167.8, 189.1, 192.9.

2-(2,6-Dioxotetrahydro-2*H*-pyran-3-yl)-1*H*-isoindole-1,3(2*H*)-dione (2). The yield was 18%. Found (%): C, 60.29; H, 2.9; N, 5.3. $C_{13}H_9NO_5$. Calculated (%): C, 60.24; H, 3.5; N, 5.4. IR, ν/cm^{-1}: 1646, 1724, 1764.

2-(1,3-Dioxo-2,3-dihydro-1*H*-isoindol-2-yl)pentanedioyl dichloride (9). The yield was 79%. Found (%): C, 49.32; H, 3.24; Cl, 22.56; N, 4.53. $C_{13}H_9Cl_2NO_4$. Calculated (%): C, 49.71; H, 2.89; Cl, 22.57; N, 4.46. IR, ν/cm^{-1}: 1646, 1795, 1798.

Synthesis of bromo ketones (general procedure). A 48% aqueous solution of HBr (1 mL) was added to a stirred solution of diazo ketone (1 mmol) in CH_2Cl_2 (10 mL). After gas evolution ceased, the solution was stirred for 1 h and the organic layer was separated, washed with 5% Na_2CO_3, and dried over $MgSO_4$. The solvent was removed and the residue was chromatographed.

Methyl 6-bromo-2-(1,3-dioxo-2,3-dihydro-1*H*-isoindol-2-yl)-5-oxohexanoate (4). The yield was 82%. Found (%): C, 49.01; H, 3.63; Br, 22.1; N, 4.23. $C_{15}H_{14}BrNO_5$. Calculated (%): C, 48.93; H, 3.83; Br, 21.7; N, 3.8. IR, ν/cm^{-1}: 1636, 1714, 1774, 1750. ^{1}H NMR, δ: 2.31—2.69, 2.71—2.79 (both m, 2 H each, CH_2); 3.69 (s, 3 H, Me); 3.85 (s, 2 H, $BrCH_2$); 4.79—4.88 (m, 1 H, CH); 7.69—7.88 (m, 4 H, C_6H_4). ^{13}C NMR, δ: 23.1, 33.9, 36.0, 50.7, 52.7, 123.7, 131.4, 134.3, 167.3, 169.0, 200.5.

2-(1,7-Dibromo-2,6-dioxoheptan-3-yl)-1*H*-isoindole-1,3(2*H*)-dione (11). The yield was 93%. Found (%): C, 41.6; H, 3.12; Br, 36.95; N, 3.2. $C_{15}H_{14}BrNO_5$. Calculated (%): C, 41.79; H, 3.04; Br, 37.07; N, 3.25. IR, ν/cm^{-1}: 1636, 1714, 1774, 1750. ^{1}H NMR, δ: 2.42—2.78, 2.60—2.68 (both m, 2 H each, CH_2); 4.12, 3.85 (both s, 2 H each, $BrCH_2$); 5.09—5.24 (m, 1 H, CH); 7.71—7.88 (m, 4 H, C_6H_4). ^{13}C NMR, δ: 23.1, 34.0, 35.9, 50.7, 52.7, 123.7, 131.4, 134.3, 167.3, 169.0, 200.5.

Methyl 6-bromo-4-(1,3-dioxo-2,3-dihydro-1*H*-isoindol-2-yl)-5-oxohexanoate (17). The yield was 99%. Found (%): C, 49.1; H, 3.54; Br, 21.5; N, 4.59. $C_{15}H_{14}BrNO_5$. Calculated (%): C, 48.93; H, 3.83; Br, 21.7; N, 3.8. IR, ν/cm^{-1}: 1636, 1714, 1774, 1750. ^{1}H NMR, δ: 2.29—2.68, 2.30—2.45 (both m, 2 H each, CH_2); 3.59 (s, 3 H, Me); 3.99 (s, 2 H, $BrCH_2$); 5.11—5.19 (m, 1 H, CH); 7.71—7.96 (m, 4 H, C_6H_4). ^{13}C NMR, δ: 23.3, 30.2, 30.9, 51.6, 55.4, 123.7, 131.4, 134.5, 167.5, 172.3, 196.4.

Synthesis of sulfonium salts (general procedure). Dimethyl sulfide (3 mmol) was added to a stirred solution of bromo ketone (1 mmol) in dry acetone (10 mL) and the mixture was kept for 12 h. The solvent was decanted and the precipitate was washed with acetone.

5-[(1,3-Dioxo-2,3-dihydro-1*H*-isoindol-2-yl)-5-methoxycarbonyl-2-oxopentyl]dimethylsulfonium bromide (5). The yield was 61%, m.p. 153—155 °C. Found (%): C, 47.46; H, 4.15; Br, 18.78; N, 3.28; S, 7.66. $C_{17}H_{20}BrNO_5S$. Calculated (%): C, 47.45; H, 4.68; Br, 18.57; N, 3.26; S, 7.45. IR, ν/cm^{-1}: 1714, 1724, 1776. ^{1}H NMR (CF_3COOH), δ: 2.82 (s, 6 H, Me); 2.24—2.57, 2.65—2.81 (both m, 2 H each, CH_2); 3.63 (s, 3 H, Me); 4.55 (s, 2 H, CH_2); 4.8—4.89 (m, 1 H, CH); 7.58—7.75 (m, 4 H, C_6H_4). ^{13}C NMR, δ: 22.5, 24.7, 37.4, 51.3, 53.6, 54.4, 124.3, 130.9, 135.6, 169.9, 171.8, 200.5.

1,7-Bis(dimethylsulfonio)-3-(1,3-dioxo-2,3-dihydro-1*H*-isoindol-2-yl)-2,6-dioxoheptane dibromide (12). The yield was 70% (hygroscopic compound). Found (%): C, 41.6; H, 4.95; Br, 28.05; N, 2.35; S, 10.8. $C_{17}H_{20}BrNO_5S$. Calculated (%): C, 41.09; H, 4.54; Br, 28.78; N, 2.52; S, 11.55. IR, ν/cm^{-1}: 1714, 1724, 1776. ^{1}H NMR (CF_3COOH), δ: 2.83 (s, 6 H, Me); 2.39—2.59, 2.52—2.81 (both m, 2 H each, CH_2); 4.52, 4.78 (both s, 2 H each, CH_2); 4.85—5.08 (m, 1 H, CH); 7.58—7.72 (m, 4 H, C_6H_4). ^{13}C NMR, δ: 25.1, 29.5, 37.7, 53.4, 54.5, 57.4, 124.6, 131.0, 135.9, 169.6, 196.1, 200.5.

3-[(1,3-Dioxo-2,3-dihydro-1*H*-isoindol-2-yl)-5-methoxycarbonyl-2-oxopentyl]dimethylsulfonium bromide (18). The yield was 69%, m.p. 130—132 °C. Found (%): C, 46.89; H, 4.16; Br, 18.71; N, 3.56; S, 7.91. $C_{17}H_{20}BrNO_5S$. Calculated (%): C, 47.45; H, 4.68; N, 3.26; Br, 18.57; S, 7.45. IR, ν/cm^{-1}: 1714, 1724, 1776. ^{1}H NMR (CF_3COOH), δ: 2.82 (s, 6 H, Me); 2.24—2.57, 2.65—2.81 (both m, 2 H each, CH_2); 3.63 (s, 3 H, Me); 4.55 (s, 2 H, CH_2); 4.80—4.89 (m, 1 H, CH); 7.58—7.75 (m, 4 H, C_6H_4). ^{13}C NMR, δ: 22.5, 24.7, 37.4, 51.3, 53.6, 54.4, 124.3, 130.9, 135.6, 169.9, 171.8, 200.5.

Synthesis of sulfur ylides by deprotonation of sulfonium salts (general procedure). Sodium hydride (1.1 mmol) was added in one portion to a stirred suspension of a sulfonium salt (3 mmol) in anhydrous THF (10 mL). The reaction mixture was stirred for 30 min, filtered, dried over K_2CO_3, and concentrated. All the ylides obtained are very unstable and decompose at room temperature.

Methyl 6-(dimethyl-λ^4-sulfanylidene)-2-(1,3-dioxo-2,3-dihydro-1*H*-isoindol-2-yl)-5-oxohexanoate (6). The yield was 86%. Found (%): C, 58.77; H, 5.01; N, 3.99; S, 9.2. $C_{17}H_{19}NO_5S$. Calculated (%): C, 58.44; H, 5.48; N, 4.01; S, 9.18. IR, ν/cm^{-1}: 1560, 1714, 1774.

2-[1,7-Bis(dimethyl-λ^4-sulfanylidene)-2,6-dioxoheptan-3-yl]-2*H*-isoindole-1,3-dione (13). The yield was 45%. Found (%): C, 58.04; H, 5.33; N, 3.6; S, 16.35. $C_{19}H_{23}NO_4S_2$. Calculated (%): C, 57.99; H, 5.89; N, 3.56; S, 16.29. IR, ν/cm^{-1}: 1540 (br), 1714, 1774.

Methyl 6-(dimethyl-λ^4-sulfanylidene)-4-(1,3-dioxo-2,3-dihydro-1*H*-isoindol-2-yl)-5-oxohexanoate (19). The yield was 82%. Found (%): C, 58.98; H, 4.85; N, 3.76; S, 8.79. $C_{17}H_{19}NO_5S$. Calculated (%): C, 58.44; H, 5.48; N, 4,01; S, 9.18. IR, ν/cm^{-1}: 1560, 1714, 1774.

Synthesis of sulfur ylides according to the carbene method (general procedure). The salt $Rh_2(OAc)_4$ (0.004 g, 0.009 mmol) was added in one portion to a stirred solution of diazo ketone (2.05 mmol) and Me_2S (1.0 g, 16.1 mmol) in dry benzene (10 mL). The reaction mixture was stirred at 80 °C until the diazo ketone disappeared (TLC, $CHCl_3$—Me_2CO (9 : 1), spot visualization with ninhydrin). The solvent was removed, toluene was added, and intramolecular cyclization was carried out.

Intramolecular cyclization. An ylide (2 mmol) was dissolved in hot dry toluene (8 mL). Then BzOH (2 mmol) was added and the mixture was refluxed for 0.5 h. The solvent was removed and the residue was chromatographed.

Methyl 2-(1,3-dioxo-2,3-dihydro-1*H*-isoindol-2-yl)-6-methylsulfanyl-5-oxohexanoate (7). The yield was 19%. Found (%): C, 57.25; H, 5.74; N, 4.84; S, 8.8. $C_{16}H_{17}NO_5S$. Calculated (%): C, 57.3; H, 5.11; N, 4.18; S, 9.56. IR, ν/cm^{-1}: 1721, 1733, 1765. ^{1}H NMR, δ: 2.02 (s, 3 H, Me); 2.39—2.73, 2.52—2.65 (both m, 2 H each, CH_2); 3.11 (s, 2 H, CH_2); 3.72 (s, 3 H, Me); 4.85—4.95 (m, 1 H, CH); 7.69—7.88 (m, 4 H, C_6H_4). ^{13}C NMR, δ: 15.5, 23.0, 36.1, 42.5, 51.0, 52.7, 123.5, 131.6, 134.2, 167.4, 169.2, 203.5.

Methyl 6-benzoyloxy-2-(1,3-dioxo-2,3-dihydro-1*H*-isoindol-2-yl)-5-oxohexanoate (8). The yield was 32%. Found (%): C, 64.29; H, 4.91; N, 2.93. $C_{22}H_{19}NO_7$. Calculated (%): C, 64.55; H, 4.68; N, 3.42. IR, ν/cm^{-1}: 1718, 1729, 1778. ^{1}H NMR, δ: 2.39—2.73, 2.52—2.65 (both m, 2 H each, CH_2); 3.72 (s, 3 H, Me); 4.82 (s, 2 H, CH_2); 4.85—4.95 (m, 1 H, CH); 7.41 (t, 2 H, *m*-H_{Ph}, J = 7.6 Hz); 7.55 (t, 1 H, *p*-H_{Ph}, J = 7.6 Hz); 7.41 (d, 2 H, *o*-H_{Ph}, J = 7.6 Hz); 7.69—7.88 (m, 4 H, C_6H_4). ^{13}C NMR, δ: 22.5, 35.1, 50.9, 52.7, 68.1, 123.5, 128.3, 128.9, 129.7, 131.5, 133.3, 134.2, 165.6, 167.4, 169.0, 202.4.

2-(2,5-Dioxocyclohept-3-enyl)isoindole-1,3(2*H*)-dione (14). The yield was 40%. Found (%): C, 66.69; H, 3.98; N, 5.21. $C_{15}H_{11}NO_4$. Calculated (%): C, 66.91; H, 4.12; N, 5.2. IR, ν/cm^{-1}: 1753, 1758, 1765. ^{1}H NMR, δ: 2.12—3.11, 2.83—2.98 (both m, 2 H each, CH_2); 4.97—4.06 (m, 1 H, CH); 6.55 (s, 2 H, CH=CH); 7.68—8.28 (m, 4 H, C_6H_4). ^{13}C NMR, δ: 24.6, 40.8, 58.7, 123.6, 131.7, 134.3, 135.3, 137.6.

Methyl 3-[1-(methylthio)-2,5-dioxo-2,5-dihydro-3*H*-pyrrolo[2,1-*a*]isoindol-3-yl]propanoate (20). The yield was 56%. Found (%): C, 59.93; H, 5.34; N, 4.44; S, 10.01. $C_{16}H_{15}NO_4S$. Calculated (%): C, 60.56; H, 5.76; N, 4.41; S, 10.10. IR, ν/cm^{-1}: 1720, 1734, 1765. ^{1}H NMR, δ: 2.19 (s, 3 H, Me); 2.32—2.65, 2.49—2.61 (both m, 2 H each, CH_2); 3.64 (s, 3 H, Me); 4.45—4.54 (m, 1 H, CH); 7.68—8.28 (m, 4 H, C_6H_4). ^{13}C NMR, δ: 15.6, 25.8, 29.2, 51.7, 60.6, 122.1, 124.3, 125.3, 130.2, 132.3, 132.8, 133, 161.8, 162.2, 172.6, 199.1.

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