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Effect of Ring Size on the *Exo*/*Endo* Selectivity of a Thermal Double Cycloaddition of Fused Pyran-2-ones

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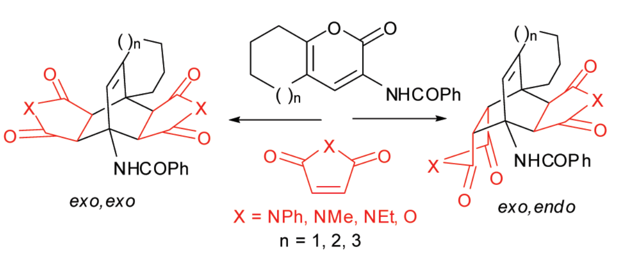

A study of an unusual effect of the size of the ring fused to 2*H*-pyran-2-ones on the *exo*/*endo* selectivity of a thermal double cycloaddition of *N*-substituted maleimides or maleic anhydride yielding bicyclo[2.2.2]octene derivatives is presented. With subtle variations of starting compounds and reaction conditions exclusively *exo*,*exo* or *exo*,*endo* products can be prepared.

The Diels−Alder reaction, as a special case of cycloadditions, is a well-established method for constructing new C−C bonds.[1] In a continuation of investigations on such reactions with a variety of 2*H*-pyran-2-ones and their fused derivatives containing a protected 3-amino group their potential use as dienes was demonstrated.[2] In such reactions maleic anhydride[2c] and *N*-substituted maleimides[2d−g] proved to be of special interest, yielding symmetrical, double cycloadducts containing the bicyclo[2.2.2]octene core or, alternatively, when a suitable dehydrogenation agent (e.g., Rh/C) was applied, benz[*e*]isoindoles[2d] have been prepared. However, so far all of these bicyclo[2.2.2]octenes obtained in thermal cycloadditions were of the type containing a plane of symmetry (*exo*,*exo*).[3] Such symmetrical *exo*,*exo* products arise through the following pathway: in the first cycloaddition step (which can take place either as an *exo* or *endo*[4] process) two enantiomeric pairs of different CO_2-bridged adducts **3** are produced. The next step involves the retro-Diels−Alder elimination of CO_2 (which includes the loss of one asymmetry element) and yields just a single enantiomeric pair of the cyclohexadiene intermediate **4**. In the second cycloaddition step (again either *exo* or *endo*, but in this case additionally also *anti* or *syn*[5]) **4** can be transformed via four enantiomeric pairs of transition states into the following possible products: an enantiomeric pair of unsymmetrical products (*exo*,*endo*) and two different symmetrical products (i.e., *exo*,*exo* **5** and *endo*,*endo*), each of the latter two being a *meso* compound (Scheme 1, not taking into account the dynamic asymmetry caused by the fused cycloalkene ring). Nevertheless, we were curious to see whether it would be possible to modify the starting fused pyran-2-ones in such a way that the second attack would take place differently, leading to products without a plane of symmetry. With this goal in mind, we embarked on a comparative investigation of the cycoadditions of a set of pyran-2-ones **1**[6] with fused rings of different sizes (6- to 8-membered rings) anticipating that an eight-membered ring, with one of its preferred boat conformations,[7] should provide the appropriate steric effects.

Initially, we carried out the reactions under conventional heating conditions in refluxing toluene; however, in some cases higher temperatures were needed, and so we applied decalin (bp 189−191 °C) or tetralin (bp 207 °C). We found that this was an appropriate way to obtain the products **5**,**6** (Schemes 1 and 2, Table 1, entries 1−7, 11, and 13), but unfortunately the reaction times were rather long and the yields a little low, due to isolation complications.

The structural elucidation of the prepared bicyclo[2.2.2]-octenes **5**,**6** indeed showed that when starting from **1A**,**B** the cycloadducts obtained with all the investigated dienophiles have a symmetric *exo*,*exo* structure **5A**,**B**. Only when starting from **1C**, where the ring fused to the pyran-2-one was eight membered, did the cycloadditions with **2a**−**c** proceed via a different stereocourse, providing the other type of bicyclo products, i.e., those with the asymmetric *exo*,*endo* structure **6**.

To improve our control of the reaction parameters, in particular the temperature, and to simplify the isolation

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(1) (a) Nicolaou, K. C.; Snyder, S. A.; Montagnon, T.; Vassilikogiannakis, G. *Angew. Chem., Int. Ed.* **2002**, *41*, 1668–1698. (b) Markó, I. E.; Evans, G. R.; Seres, P.; Chellé, I.; Janousek, Z. *Pure Appl. Chem.* **1996**, *68*, 113–122.

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(4) *Endo* addition involves the tendency for dienophile substituents to be so oriented in the favored transition state that they lie directly above the residual unsaturation of the diene (see: Martin, J. G.; Hill, R. K. *Chem. Rev.* **1961**, *61*, 537–562).

(5) *Syn* being defined as an attack from the same side of the diene system as the previously incorporated dienophile ring is located. Conversely, *anti* means from the other side.

(6) For the synthesis of the starting compounds **1**, see: Požgan, F.; Kranjc, K.; Kepe, V.; Polanc, S.; Kočevar, M. *ARKIVOC* **2007**, *8*, 97–111.

(7) (a) Anet, F. A. L. *Top. Curr. Chem.* **1974**, *45*, 169–220. (b) Romines, K. R.; Morris, J. K.; Howe, W. J.; Tomich, P. K.; Horng, M.-M.; Chong, K.-T.; Hinshaw, R. R.; Anderson, D. J.; Strohbach, J. W.; Turner, S. R.; Mizsak, S. A. *J. Med. Chem.* **1996**, *39*, 4125–4130.

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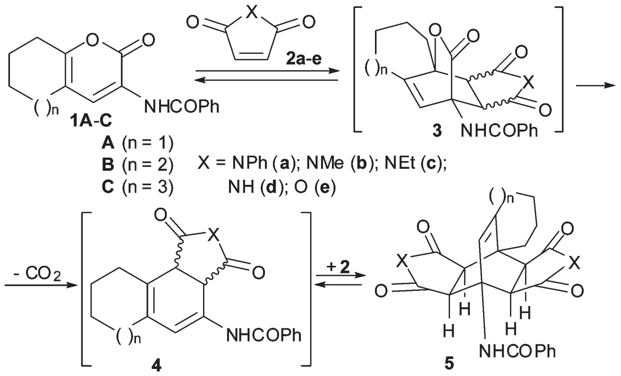
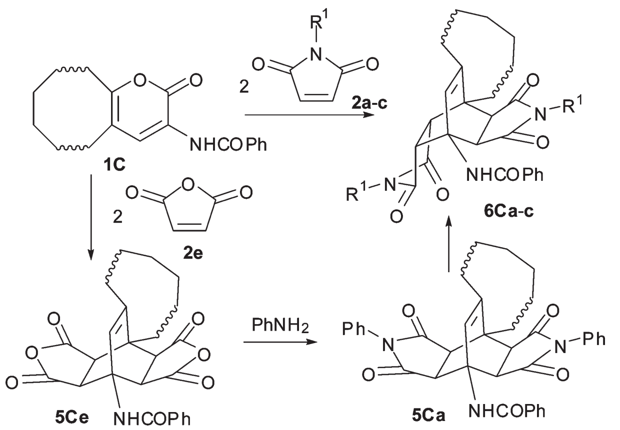
SCHEME 1. General Pathway of Cycloadditions Yielding the Symmetrical *Exo*,*Exo* Products 5



SCHEME 2. Cycloaddition on Pyran-2-One with a Fused Eight-Membered Ring Yielding Either the *Exo*,*Endo* (6) or *Exo*,*Exo* (5) Products

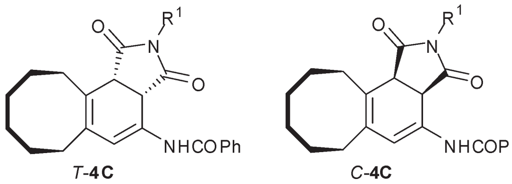


procedure as a consequence of circumventing the use of high-boiling-point solvents, we decided to investigate some of these transformations as neat reactions under microwave-irradiation conditions.[8] As the model reaction, a mixture of the starting pyran-2-one **1C** and *N*-phenylmaleimide (**2a**) in the molar ratio 1:2.2 together with a minor amount of toluene (100 mg) indeed provided the desired *exo*,*endo* adduct **6Ca**; however, after a short irradiation time (1−30 min) at 100 °C there was also an appreciable amount (30−40%) of another product detected in the crude reaction mixture (Scheme 2, Table 1, entries 8 and 9). We surmised that this secondary product might be the symmetrical *exo*,*exo* adduct **5Ca** (as was proved in subsequent experiments, see below). To obtain the pure adduct **6Ca** and to circumvent the appearance of the product **5Ca** it was necessary to irradiate the reaction mixture of **1C** and **2a** for a longer time (90 min) and at a higher temperature (180 °C) (Table 1, entry 10). Analogous conditions were appropriate for the preparation of **6Cb** and **6Cc** (Table 1, entries 12 and 14). Additionally, irradiation of the pure adduct **5Ca** (of the *exo*,*exo* structure) at 220 °C for 3 h yielded, with a complete conversion, the *exo*,*endo* product **6Ca** (accompanied by a small amount of the aromatized product **7Ca**).

TABLE 1. Reaction Conditions and Yields for the Synthesis of 5−7

entry	starting compounds **1**	*n*	**2**	X	product	structure	*t*/h	yield (%)^a
1	**1A**	1	**2a**	NPh	**5Aa**	*exo*,*exo*	0.5^b	67
2	**1A**	1	**2b**	NMe	**5Ab**	*exo*,*exo*	9^c	62
3	**1A**	1	**2c**	NEt	**5Ac**^{2d}	*exo*,*exo*	2.5^c	61
4	**1A**	1	**2d**	NH	**5Ad**	*exo*,*exo*	3^c	65
5	**1B**	2	**2b**	NMe	**5Bb**	*exo*,*exo*	2.5^c	78
6	**1B**	2	**2d**	NH	**5Bd**	*exo*,*exo*	3.25^c	75
7	**1C**	3	**2a**	NPh	**6Ca**	*exo*,*endo*	4^b	77
8	**1C**	3	**2a**	NPh	**6Ca**:**5Ca**		0.1^{d,e}	1:0.35
9	**1C**	3	**2a**	NPh	**6Ca**:**5Ca**		0.5^{d,e}	1:0.35
10	**1C**	3	**2a**	NPh	**6Ca**	*exo*,*endo*	1.5^{e,f}	90
11	**1C**	3	**2b**	NMe	**6Cb**	*exo*,*endo*	6^b	71
12	**1C**	3	**2b**	NMe	**6Cb**	*exo*,*endo*	1.5^{f,g}	86
13	**1C**	3	**2c**	NEt	**6Cc**	*exo*,*endo*	4^b	82
14	**1C**	3	**2c**	NEt	**6Cc**	*exo*,*endo*	1.5^{f,g}	92
15	**1C**	3	**2e**	O	**5Ce**	*exo*,*exo*	0.5^h	68
16	**1C**	3	**2e**	O	**7Ce**		1^i	89

[a] Yield of isolated products. [b] Reflux in decalin. [c] Reflux in toluene. [d] Microwave irradiation in a closed vessel (10 mL) at 100 °C. [e] With the addition of 100 mg (1.1 mmol) of toluene. [f] The same as *d*, only at 180 °C. [g] At 180 °C and with the addition of 100 mg (1.35 mmol) of butan-1-ol. [h] Reflux in tetralin. [i] The same as *d*, only at 200 °C.



T-**4C** *C*-**4C**

FIGURE 1. Two different forms of the intermediate **4Ca−c** (each exists as a pair of enantiomers).

The number of intermediates and transition states in the cycloaddition pathway starting from **1C** is doubled in comparison with the case described above for **1A**,**B**, because **1C** contains an eight-membered ring, adding an element of dynamic asymmetry. Therefore, the first cycloaddition step can produce four enantiomeric pairs of the CO_2-bridged systems **3C**, which are, after the elimination of CO_2, transformed into two enantiomeric pairs of the cyclohexadiene intermediates **4C** (termed *T*- and *C*-type,[9] Figure 1). It is worth pointing out that with the flipping of the eight-membered ring some of these isomers can interconvert. The second cycloaddition step can subsequently take place via eight enantiomeric pairs of transition states. It is important to note that the *endo*−*anti* attack is the only possible pathway leading to a symmetric *exo*,*exo* product. This attack, of course, can happen either on the *T*-**4C** or *C*-**4C**; however, on the basis of sterical hindrances evident in such an attack on the *T*-**4C** it is, energetically speaking, exceedingly demanding. The most probable possibility for obtaining the *exo*,*exo* product **5C** is therefore via *C*-**4C**, whereas

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(8) (a) *Microwaves in Organic Synthesis*; Loupy, A., Ed.; Wiley-VCH: Weinheim, Germany, 2002. (b) Hayes, B. L. *Microwave Synthesis: Chemistry at the Speed of Light*; CEM: Matthews, NC, 2002. (c) Lidström, P.; Tierney, J.; Wathey, B.; Westman, J. *Tetrahedron* **2001**, *57*, 9225–9283. (d) de la Hoz, A.; Díaz-Ortiz, A.; Moreno, A. *Chem. Soc. Rev.* **2005**, *34*, 164–178. (e) Martelanc, M.; Kranjc, K.; Polanc, S.; Kočevar, M. *Green Chem.* **2005**, *7*, 737–741. (f) Dallinger, D.; Kappe, C. O. *Chem. Rev.* **2007**, *107*, 2563–2591. (g) Polshettiwar, V.; Varma, R. S. *Chem. Soc. Rev.* **2008**, *37*, 1546–1557. (h) Kappe, C. O.; Dallinger, D. *Mol. Diversity* **2009**, *13*, 71–193.

(9) The *C*-form (*cisoid*) of the intermediate **4C** is defined as the one where the ring of dienophile is on the same side of the diene system as the cyclooctene ring is bent to. In the *T*-form (*transoid*) one ring is on the opposite side. See Figure 1.

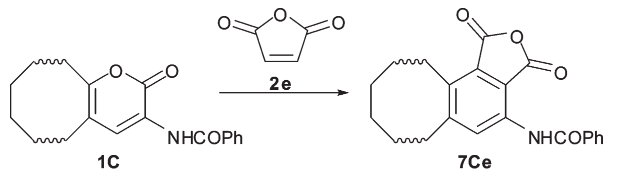
T-**4C** reacts via another, energetically favorable possibility (probably via *endo*–*syn* attack), into the unsymmetrical *exo*,*endo* product **6C**. It is appropriate to assume that **6C** is thermodynamically more stable than **5C** (by approximately 5.6 kcal/mol, according to AM1 and PM3);[10] **5C** therefore represents the kinetically favored product, thus corroborating the experimental results (Table 1, entries 8–10). However, in the case when six- or seven-membered rings are fused to the pyran-2-one (i.e., **1A** and **1B**) the thermodynamically more stable products according to AM1 and PM3 calculations are the symmetrical *exo*,*exo* **5A** and **5B** (and not *exo*,*endo* **6A** and **6B** as in the previous case) by approximately 4.9 and 3.2 kcal/mol, respectively.

The cycloadditions of maleic anhydride (**2e**) with **1A**,**B**, having a six- or seven-membered ring fused to pyran-2-one, were already investigated, and were found to yield the symmetrical *exo*,*exo* adducts (**5Ae** and **5Be**).[2c] On the other hand, we expected that with the eight-membered fused pyran-2-one **1C** the asymmetric *exo*,*endo* adduct would be obtained (**6Ce**). However, it turned out that in this case we obtained exclusively the symmetrical *exo*,*exo* product **5Ce** (Scheme 2, Table 1, entry 15).

The adduct **5Ce** can be easily transformed with aniline under microwave irradiation (1.25 h, 160 °C) into the derivative **5Ca**, having significantly different spectroscopic properties than **6Ca**, and thus evidently being its stereoisomer. Product **5Ca**, obtained in this way, was used as a comparison with the side product of the microwave-irradiated reaction between **1C** and **2a** (Table 1, entries 8 and 9), thus unequivocally proving that the side product in these cases was indeed the symmetrical *exo*,*exo* adduct **5Ca**.[11]

On the other hand, when a neat mixture of **1C** and maleic anhydride (**2e**) was irradiated with microwaves at a higher temperature and for a longer time (Scheme 3, Table 1, entry 16), the product obtained was the aromatized cycloocta[*e*][2]-benzofuran **7Ce** and not the *exo*,*endo* double adduct **6Ce**, as one might expect. Obviously, under such severe conditions the aromatization[12] of **4Ce** becomes the preferred path. Unfortunately, all our attempts so far to produce an *exo*,*endo* product **6Ce** have proved to be futile.

SCHEME 3. Preparation of the Aromatized Cycloadduct 7Ce



1C **7Ce**

The difference between the two types of structures, **5** and **6**, could be relatively easily inferred from the ^{1}H and ^{13}C NMR spectra. For the *exo*,*exo* structures **5**, in the ^{1}H NMR spectrum two sets of doublets (J = 8.0–8.6 Hz), each integrated as 2 H at 2.92–3.59 (9b-H/10-H, 10b-H/11-H, and 11b-H/12-H for six-, seven-, and eight-membered rings, respectively) and 4.10–4.57 (3a-H/14-H, 3a-H/15-H, and 3a-H/16-H for six-, seven-, and eight-membered rings, respectively), were observed, belonging to the four aliphatic protons of the bicyclo[2.2.2]octene skeleton,[13] thus implying the symmetric structure. For the *exo*,*endo* structures **6**, on the other hand, for the same aliphatic protons of the bicyclo[2.2.2]octene skeleton four sets of doublets (each integrated as 1 H) were observed at 2.69–3.18 and 3.37–4.66 for 3a-H/11b-H and 12-H/16-H, respectively, clearly showing that these are no longer symmetric. The coupling constant for the two sets of protons is also markedly different: for the set of protons 3a-H/11b-H (which are *endo* to the double bond) it is 7.4–8.0 Hz, whereas for the other set of protons 12-H/16-H (which are *exo* to the double bond) it is 9.9–10.4 Hz. It is of interest to note that **5Ce** gives a symmetric spectrum (exactly like the other products **5**), proving that the dynamics on the NMR time scale of the eight-membered ring in solution at room temperature is fast. The loss of symmetry between the two types of products (**5** vs. **6**) can also be concluded after an analysis of the ^{13}C NMR spectra. The definitive answer regarding the correct stereo structure of the presented bicyclo[2.2.2]octenes, however, was obtained from the X-ray diffraction studies (see Figures 1 and 2 in the Supporting Information), which clearly confirmed the conclusions drawn from the NMR studies.

The presented results are very interesting, as it was not possible to anticipate (at least not from previous literature reports) that the interplay between the size of the ring (**1A**,**B** vs. **1C**), the type and size of the substituent on the cyclic dienophile **2** (NR^1 vs. O), and the stabilities of products would have such a strong effect on the stereo outcome of these thermal cycloadditions. Similar *exo*,*endo* products were so far obtained only under photochemical conditions;[14] however, an effect of the structure of the starting compounds on the stereo outcome of the cycloaddition was not reported; only the effects of various reaction conditions were presented.

In our future research we will try to elucidate in detail the reasons for this unusual phenomenon and, with appropriate calculation methods, provide a further insight into our simple, qualitative explanation described above. In this way we might be able to anticipate additional reactions of this type.

Experimental Section[15]

Microwave-Assisted Synthesis of the Products 6 and 7. A mixture of the starting fused pyran-2-one **1** (1 mmol) and

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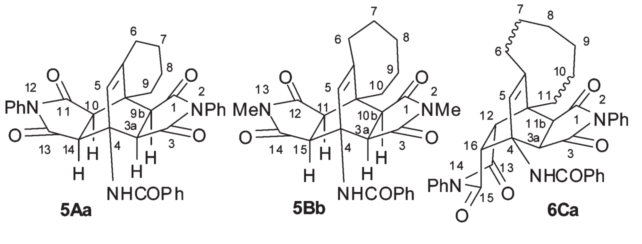
(10) Frisch, M. J.; et al. et al. *Gaussian 03*, Revision B.03; Gaussian, Inc., Wallingford, CT, 2004.

(11) According to AM1 and PM3 calculations, *exo*,*endo* adduct **6Ce** is thermodinamcally more stable than *exo*,*exo* adduct **5Ce** by approximately 5 kcal/mol. Therefore, this process seems to take place under kinetic control yielding the adduct via the *endo*,*anti* attack.

(12) Aromatization takes place via the transfer of hydrogen to the **2e**, thus forming succinic anhydride (for a related case forming substituted succinimides from maleimides, as observed previously, see ref 2d).

(13) Numbering sequences for compounds **5Aa**, **5Bb**, and **6Ca** are the following:



5Aa **5Bb** **6Ca**

(14) (a) Obata, T.; Shimo, T.; Yoshimoto, S.; Somekawa, K.; Kawaminami, M. *Chem. Lett.* **1999**, 181–182. (b) Shimo, T.; Matsushita, M.; Omar, H. I.; Somekawa, K. *Tetrahedron* **2005**, *61*, 8059–8064.

(15) For the other general experimental details and characterization data for all synthesized compounds, see the Supporting Information.

dienophile **2** (2.2 mmol) with the addition of a liquid additive (100 mg; toluene (1.1 mmol) or butan-1-ol (1.35 mmol)) or alternatively without (in the case of synthesis of **7**) was irradiated in the focused microwave equipment for the specified time (Table 1). The final temperature was set to 180 °C (or 200 °C in the case of **7**), the power to 150 W (or 100 W in the case of **7**), and the ramp time to 5 min. Thereafter, the reaction mixture was cooled to room temperature and the volatile components were removed in vacuo, the remaining solid was treated with a minimal amount of EtOH/H_2O (1 mL) and then it was cooled in a refrigerator. The precipitated product was filtered off and washed with EtOH/H_2O.

***N*-[*rel*-(3a*R*,11b*S*,12*S*,16*R*)-2,3,3a,6,7,8,9,10,11,11b,13,14,15,16-Tetradecahydro-1,3,13,15-tetraoxo-2,14-diphenyl-12*H*-4,11a[3′,4′]-*endo*-pyrrolocyclooct[*e*]isoindol-4(1*H*)-yl]benzamide (6Ca):**[13] yield 540 mg (90%), mp 254−256 °C (EtOH); IR (KBr) ν 1774, 1715, 1665, 1533 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.45 (m, 1H), 1.59 (m, 4H), 1.74 (m, 1H), 1.92 (m, 1H), 2.07 (m, 1H), 2.41 (m, 3H), 2.85 (m, 1H), 3.10 (d, *J* = 7.9 Hz, 1H), 3.18 (d, *J* = 7.9 Hz, 1H), 3.63 (d, *J* = 10.4 Hz, 1H), 4.66 (d, *J* = 10.4 Hz, 1H), 6.29 (s, 1H), 7.12 (m, 2H), 7.28 (m, 2H), 7.44 (m, 9H), 7.90 (m, 2H), 8.05 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ (ppm) 25.7, 26.2, 26.3, 28.9, 31.0, 31.6, 43.1, 44.2, 44.7, 45.0, 47.5, 57.7, 126.1, 126.2, 127.1, 128.6, 128.9, 129.2, 129.3, 131.0, 131.1, 131.3, 131.8, 134.2, 147.8, 167.5, 174.0, 174.1, 174.9, 175.4 (1 signal is hidden); MS-EI *m*/*z* 599 (M$^+$, 1%), 105 (100). Anal. Calcd for $C_{37}H_{33}N_3O_5$: C, 74.11; H, 5.55; N, 7.01. Found: C, 73.90; H, 5.47; N, 7.04.

***N*-[*rel*-(3a*R*,11b*S*,12*S*,16*R*)-2,3,3a,6,7,8,9,10,11,11b,13,14,15,16-Tetradecahydro-2,14-dimethyl-1,3,13,15-tetraoxo-12*H*-4,11a-[3′,4′]-*endo*-pyrrolocyclooct[*e*]isoindol-4(1*H*)-yl]benzamide (6Cb):** yield 410 mg (86%), mp 285−286 °C (EtOH); IR (KBr) ν 1767, 1699, 1668, 1528 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm) 1.29 (m, 2H), 1.48 (m, 3H), 1.68 (m, 2H), 1.97 (m, 2H), 2.19 (m, 2H), 2.78 (m, 1H), 2.74 (s, 3H), 2.78 (d, *J* = 7.6, 1H), 2.82 (s, 3H), 3.06 (d, *J* = 7.6, 1H), 3.42 (d, *J* = 9.9, 1H), 3.98 (d, *J* = 9.9, 1H), 6.00 (s, 1H), 7.59 (m, 3H), 7.88 (m, 2H), 8.34 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ (ppm) 24.9, 25.0, 25.7, 26.2, 26.3, 29.1, 30.5, 31.5, 42.8, 44.4, 44.9, 47.7, 57.4, 127.1, 128.7, 130.6, 131.8, 134.3, 147.5, 167.4, 175.1, 175.2, 176.1, 176.3 (1 signal is hidden); MS-EI *m*/*z* 475 (M$^+$, 1%), 105 (100). Anal. Calcd for $C_{27}H_{29}N_3O_5$: C, 68.19; H, 6.15; N, 8.84. Found: C, 67.98; H, 6.33; N, 8.80.

***N*-[*rel*-(3a*R*,11b*S*,12*S*,16*R*)-2,14-Diethyl-2,3,3a,6,7,8,9,10,11,11b,13,14,15,16-tetradecahydro-1,3,13,15-tetraoxo-12*H*-4,11a[3′,4′]-*endo*-pyrrolocyclooct[*e*]isoindol-4(1*H*)-yl]benzamide (6Cc):** yield 461 mg (92%), mp 233−236 °C (EtOH); IR (KBr) ν 1766, 1699, 1667, 1523 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.05 (t, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.2 Hz, 3H), 1.40 (m, 2H), 1.53 (m, 2H), 1.65 (m, 2H), 1.88 (m, 1H), 2.03 (m, 1H), 2.19 (m, 2H), 2.39 (m, 1H), 2.72 (m, 1H), 2.69 (d, *J* = 8.0 Hz, 1H), 2.76 (d, *J* = 8.0 Hz, 1H), 3.37 (d, *J* = 10.2 Hz, 1H), 3.45 (q, *J* = 7.2 Hz, 2H), 3.54 (q, *J* = 7.2 Hz, 2H), 4.42 (d, *J* = 10.2 Hz, 1H), 6.07 (s, 1H), 7.51 (m, 3H), 7.94 (m, 2H), 8.02 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ (ppm) 12.9, 13.0, 25.7, 26.2, 26.3, 29.0, 30.8, 31.6, 33.7, 33.9, 42.8, 44.1, 44.6, 44.8, 47.1, 57.5, 127.2, 128.7, 130.8, 131.8, 134.4, 147.4, 167.4, 174.9, 175.0, 175.8, 176.1; MS-EI *m*/*z* 503 (M$^+$, 3%), 105 (100). Anal. Calcd for $C_{29}H_{33}N_3O_5$: C, 69.17; H, 6.60; N, 8.34. Found: C, 69.12; H, 6.41; N, 8.47.

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Supporting Information Available: Typical experimental procedures, characterization data, copies of ^{1}H and ^{13}C NMR spectra for all synthesized compounds (**5Aa**, **5Ab**, **5Ad**, **5Bb**, **5Bd**, **6Ca**, **6Cb**, **6Cc**, **5Ce**, **5Ca**, and **7Ce**), the results of semiempirical calculations (together with the atom coordinates), and crystal data with ORTEP drawings for compounds **5Ac** and **6Cc**, as well as the corresponding CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.