Dioxopyrrolines. LXI.[1] Cycloaddition Reaction of 4-Benzoyl-5-ethoxycarbonyl-1-phenyl-1*H*-pyrrole-2,3-dione with 1,3-Dienes: Competitive Occurrence of Normal and Hetero Diels–Alder Reaction and Claisen Rearrangement of the Hetero Diels–Alder Product[2]

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Thermal cycloaddition reaction of 4-benzoyl-5-ethoxycarbonyl-1*H*-pyrrole-2,3-dione (dioxopyrroline) 1 with 1,3-dienes caused two types of Diels–Alder (D–A) reaction in a competitive manner. One is the hetero D–A reaction in which dioxopyrroline acts as an electron-deficient diene and the 1,3-diene acts as an electron-rich dienophile. The other is the normal D–A reaction in which dioxopyrroline acts as an electron-deficient dienophile. The 1,3-dienes bearing electron-rich substituents undergo the D–A reaction *via* the normal pathway, while the 1,3-dienes which do not bear an electron-donating group predominantly undergo the hetero D–A reaction. When the normal D–A pathway is sterically hindered, the hetero D–A pathway occurs exclusively.

Key words 1*H*-pyrrole-2,3-dione; dioxopyrroline; hetero Diels–Alder reaction; normal Diels–Alder reaction; Claisen rearrangement

In a preceding paper[1] we reported that 4-benzoyl-5-ethoxycarbonyl-1-phenyl-1*H*-pyrrole-2,3-dione **1** (benzoyl-dioxopyrroline) underwent a hetero Diels–Alder (D–A) reaction with olefins bearing electron-donating substituents in a highly regio- and stereoselective manner to give pyranopyrrole derivatives **2**, thus presenting an example of a D–A reaction with inverse electron demand in which the electron-deficient dioxopyrroline acts as a diene and the electron-rich olefin does as a dienophile. In this paper we show that the thermal reaction of **1** with 1,3-dienes results in two types of D–A reaction in a competitive manner; one is a hetero D–A reaction and the other is a normal D–A reaction.[2]

Results and Discussion

The D–A reaction of **1** with butadiene, by heating a toluene solution of **1** and butadiene at 100 °C for 9 h in a sealed tube, gave two adducts **3a** and **4a** in yields of 40% and 10%. The spectral data of **3a** and **4a** showed features characteristic of pyranopyrrole and hydroindole, respectively (see Experimental). Thus, the major product **3a** is an adduct of the hetero D–A reaction in which the dioxopyrroline acts as a heterodiene and butadiene as a dienophile, and the minor product **4a** is an adduct of the normal D–A reaction in which the dioxopyrroline acts as a dienophile and butadiene as an enophile.

The product ratio of **3a** and **4a** in the D–A reaction varied depending on the reaction temperature. At higher temperature (160 °C) the major product was the normal D–A adduct **4a** (66%) and the minor one was the hetero D–A adduct **3a** (7%). On the other hand, at lower temperature (90 °C) the reaction gave **3a** in 18% yield and **4a** in a negligible amount (< 1%).

The reaction of **1** with (*E*)- and (*Z*)-1,3-pentadienes gave an interesting result. (*E*)-1,3-Pentadiene, on heating in toluene at 100 °C for 6 h, gave the normal D–A adduct **4b** as a major product (69%) and the hetero D–A adduct **3b** as a minor product (15%). The structure and stereochemistry of **4b** were unambiguously determined by X-ray crystallographic analysis, confirming that the stereochemistry of 4-Me is *endo* (α-configuration) (Fig. 1). In contrast to this result, (*Z*)-1,3-pentadiene on heating in toluene at 100 °C for 24 h gave the hetero D–A adduct **3c** as a sole product (73%).

The D–A reaction of **1** with 1-substituted butadienes bearing an electron-donating group afforded the normal D–A adduct regardless of the reaction temperature. Thus, 1-trimethylsilyloxybutadiene, 1-phenylthiobutadiene, and 1-acetoxybutadiene gave the normal D–A adducts **5a—c** at 80 °C as sole products in 68%, 70%, and 46% yields, respectively. In the reaction at room temperature (20 °C), they also gave the normal D–A adducts as sole products in lesser yields (67% for **5a**, 45% for **5b**, and 24% for **5c**). Furthermore, the D–A reaction of 1-phenylthiobutadiene proceeded at −20 °C to give the same adduct **5b**, though the yield was only 19%. In these cases the product **6** from the hetero D–A pathway was not formed in any detectable amount.

The stereochemistry of 4-SPh in **5b** was determined as *endo* by an X-ray analysis (Fig. 2). The stereochemistry of 4-OTMS in **5a** and that of 4-OAc in **5c** were assigned as *endo* since the coupling pattern of 4-H in their ^{1}H-NMR spectra was similar to that of **5b**.

Next, we examined the reaction of **1** with 2-substituted 1,3-butadienes. Isoprene on heating at 100 °C for 18 h gave the normal D–A adduct **9** as a major product (67%), and two regioisomeric hetero D–A adducts **7** (7%) and **8** (14%) as minor products. The reaction of **1** with 2-

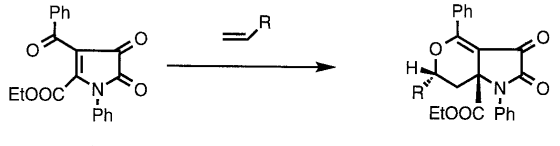

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Chart 1

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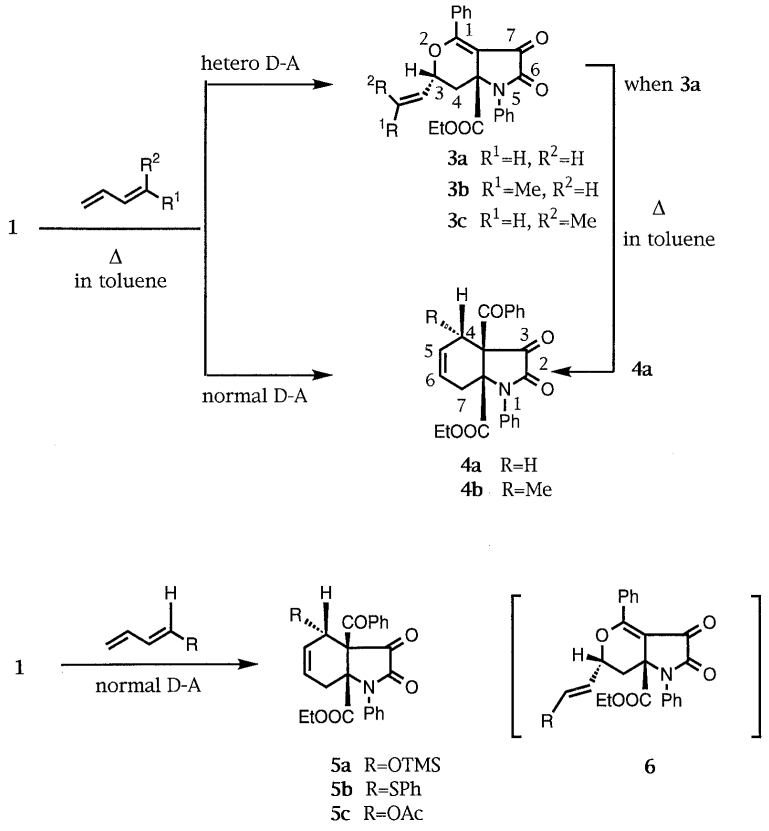

Chart 2

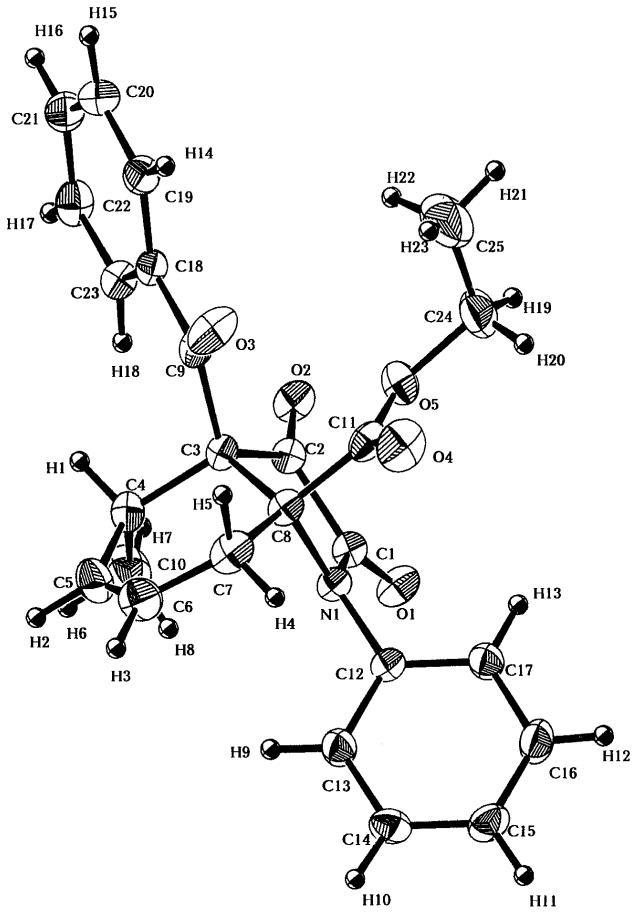

Fig. 1. Normal D–A Adduct **4b**

trimethylsilyloxybutadiene at 100 °C, after chromatographic purification over silica gel, gave three products, **10**, **11** and **12**, in 24%, 40% and 14% yields. Compounds **11** and **12** were proved to be the normal D–A adduct and its hydrolysate, respectively, while **10** was proved to have a structure derived from the hetero D–A adduct **13**. Thus, 2-substituted butadienes underwent both types of D–A reaction, though the normal D–A pathway was predominant.

These results, collected in Table 1, indicate that the 1,3-dienes with electron-donating substituents (Me, OTMS, SPh, OAc) tend to yield the normal D–A adduct, while the dienes which do not bear an electron-donating group and the sterically hindered dienes ((*Z*)-1,3-pentadiene) tend to yield the hetero D–A adduct.

As described above, in the D–A reaction of **1** with butadiene the major product at 90 °C was the hetero D–A adduct **3a** and at 160 °C the major product was the normal D–A adduct **4a**. These results imply that the normal D–A adduct can be formed *via* [3,3] sigmatropic rearrangement of the hetero D–A adduct (Claisen rearrangement). Heating of **3a** at 160 °C (8 h) in toluene gave the hydroindole **4a** in 83% yield. However, at 100 °C, the temperature of the D–A reaction described above, **3a** was recovered unchanged after 20 h.

Similarly, the hetero D–A adducts **7** and **8** from isoprene underwent the Claisen rearrangement at 160 °C to give the hydroindole **9** (61%) and **14** (82%), respectively. The Claisen product **9** was identical with the normal D–A adduct from the D–A reaction of **1** and isoprene, but the other Claisen product **14**, a regioisomer of **9**, was not detected in the crude D–A products (TLC and ^{1}H-NMR

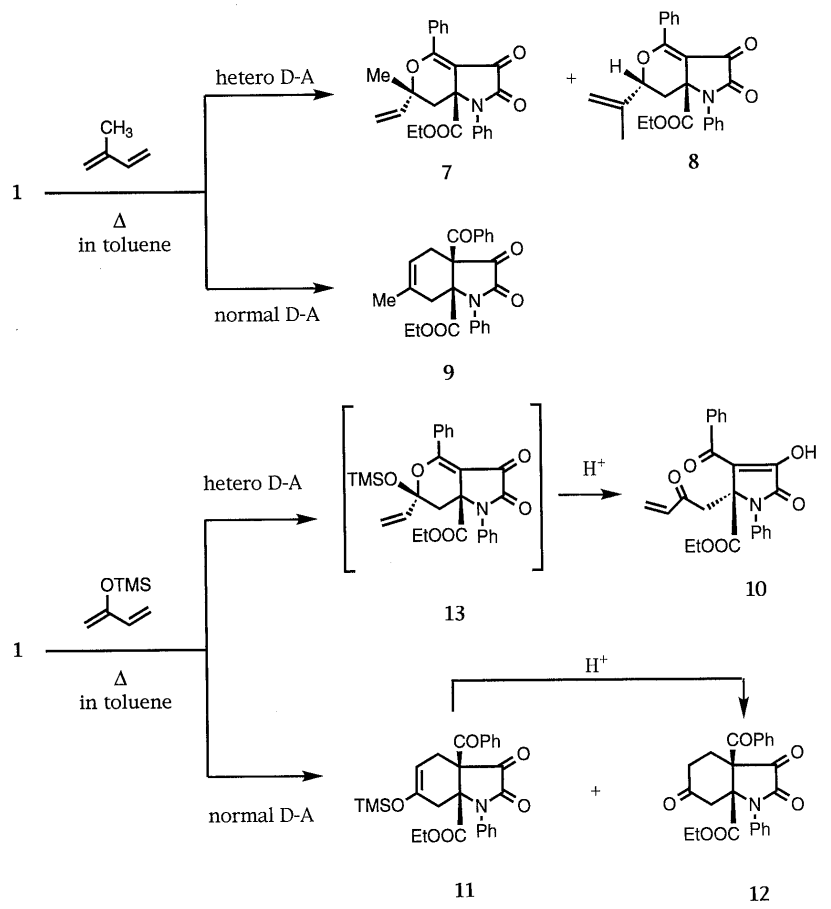

Chart 3

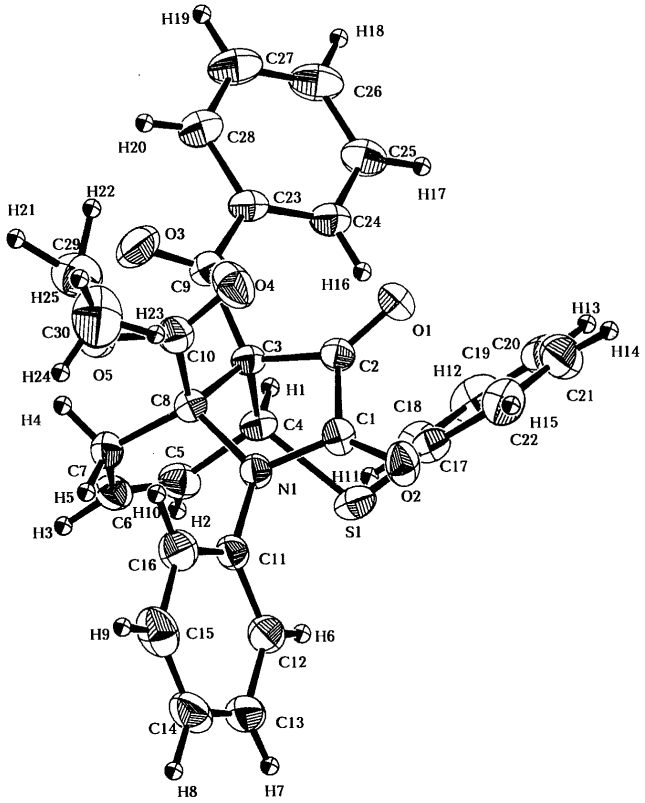

Fig. 2. Normal D–A Adduct **5b**

Table 1. Diels–Alder Reaction of **1** with 1,3-Dienes

Run	1,3-Diene	Conditions		Yields (%)	
		Temp. (°C)	Time (h)	Hetero D–A	Normal D–A
1	Butadiene	160	5.5	7 (**3a**)	66 (**4a**)
2	Butadiene	100	9	40 (**3a**)	10 (**4a**)
3	Butadiene	90	48	18 (**3a**)	Trace (**4a**)
4	Butadiene	20	86	5 (**3a**)	—
5	(*E*)-1,3-Pentadiene	100	6	15 (**3b**)	69 (**4b**)
6	(*Z*)-1,3-Pentadiene	100	24	73 (**3c**)	—
7	1-OTMS-butadiene	80	0.25	—	68 (**5a**)
8	1-OTMS-butadiene	20	2	—	67 (**5a**)
9	1-SPh-butadine	80	5	—	70 (**5b**)
10	1-SPh-butadine	20	72	—	45 (**5b**)
11	1-SPh-butadine	−20	150	—	19 (**5b**)
12	1-OAc-butadiene	80	3.5	—	46 (**5c**)
13	1-OAc-butadiene	20	150	—	24 (**5c**)
14	Isoprene	100	18	7 (**7**) 14 (**8**)	67 (**9**)
15	2-OTMS-butadiene	100	0.7	24 (**10**)	40 (**11**) 14 (**12**)
16	Cyclopentadiene	20	1	89 (**17**)	
17	Cyclopentadiene	−60	15	60 (**17**)	
18	Cyclohexadiene	120	4	90 (**18**)	

analyses).

The Claisen reaction of **3b** and **3c** gave interesting results. The hetero D–A adduct **3b** from (*E*)-pentadiene underwent the Claisen rearrangement in a stereoselective manner at a relatively low temperature (100 °C) to give the hydroindole **15** in 86% yield after 20 h. This Claisen product **15** was not identical with **4b** but was proved to

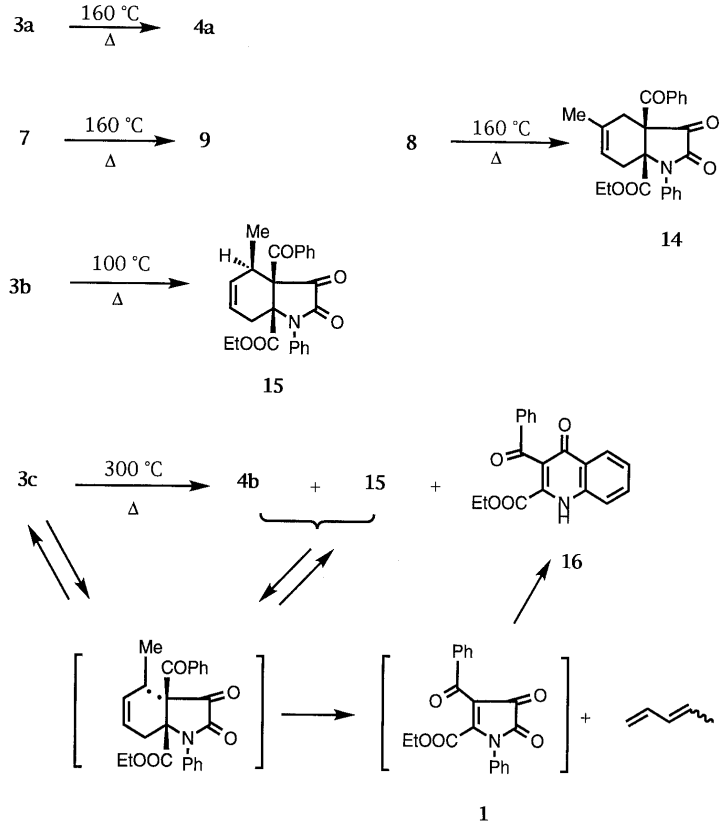

Chart 4

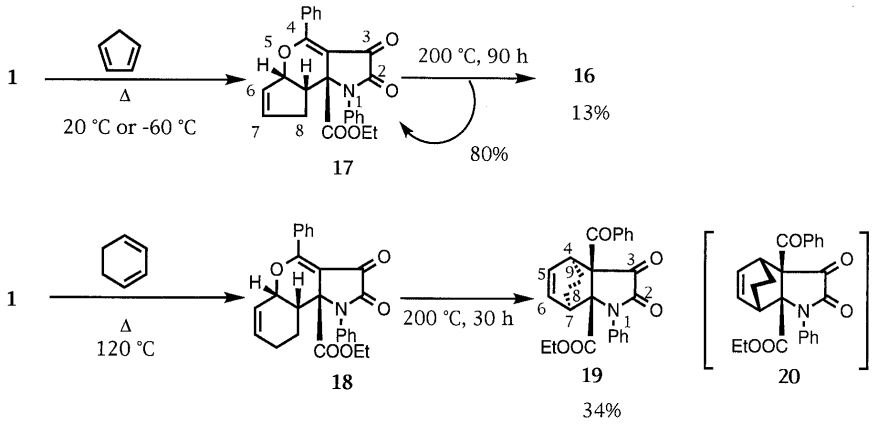

Chart 5

be the stereoisomer in respect of 4-Me. On the other hand, the Claisen rearrangement of the hetero D–A adduct **3c** from (*Z*)-pentadiene required a higher temperature. Thus, heating of **3c** at 300 °C for 65 h gave a 1 : 4 mixture of **4b** and **15** in 38% yield with recovery of the starting material (38%). Upon prolonged reaction (90 h), the ratio of **4b**/**15** was changed (1/2) and the 4-quinolone **16**, a pyrolyzate of benzoyl-dioxopyrroline **1**,[1,3] was obtained in 46% yield. The results indicated that the Claisen reaction of **3b** proceeded stereoselectively while that of **3c** did so non-stereoselectively. The formation of products from **3c** could be rationalized in terms of cycloreversion reaction, as shown in Chart 4.

From the facts that i) the Claisen rearrangement requires a higher temperature than the corresponding D–A reaction does, ii) the hydroindole **14**, the regioisomer of the D–A adduct **9**, was not formed in the D–A reaction, and iii) the Claisen product **15** (*exo* 4-Me) is a stereoisomer of the D–A adduct **4b** (*endo* 4-Me), it can be concluded that the normal D–A adduct was not a Claisen product of the hetero D–A adduct, but a direct product of the D–A reaction. The adducts **5** from 1-substituted butadienes can be concluded to be the direct product of the D–A reaction and not the Claisen product of the corresponding hetero D–A adduct **6**, which had been suggested in the preliminary communication,[2] since if **5b** is a Claisen product from **6b**, the *endo* configuration of 4-SPh in **5b** should be *exo*, as in the Claisen rearrangement of **3b** to **15**.

The D–A reaction of **1** with cyclic 1,3-dienes proceeds exclusively in the hetero D–A manner, as in the reaction of (*Z*)-pentadiene. Cyclopentadiene added to **1** at room temperature to give the hetero D–A adduct **17** in 89%

Table 2. Positional Parameters and B_{eq} for **4b**

Atom	x	y	z	B_{eq}
O(1)	0.22421 (8)	0.0882 (2)	0.53230 (7)	3.98 (7)
O(2)	0.07289 (8)	0.1367 (2)	0.52379 (7)	3.86 (7)
O(3)	0.03786 (8)	0.3647 (2)	0.67726 (8)	4.9 (8)
O(4)	0.1946 (1)	0.4702 (2)	0.66563 (9)	5.7 (1)
O(5)	0.13888 (8)	0.3893 (1)	0.57935 (7)	4.00 (7)
N(1)	0.21595 (8)	0.1739 (2)	0.63070 (7)	2.93 (7)
C(1)	0.1909 (1)	0.1337 (2)	0.5732 (1)	2.96 (9)
C(2)	0.11101 (1)	0.1503 (2)	0.5705 (1)	2.89 (9)
C(3)	0.0909 (1)	0.1804 (2)	0.63759 (9)	2.86 (8)
C(4)	0.0778 (1)	0.0490 (2)	0.6717 (1)	3.9 (1)
C(5)	0.1120 (2)	0.0424 (3)	0.7367 (1)	5.1 (1)
C(6)	0.1544 (2)	0.1277 (3)	0.7634 (1)	5.1 (1)
C(7)	0.1732 (1)	0.2490 (3)	0.7339 (1)	4.3 (1)
C(8)	0.1609 (1)	0.2474 (2)	0.66306 (9)	3.02 (9)
C(9)	0.0277 (1)	0.2707 (2)	0.6448 (1)	3.2 (1)
C(10)	0.0967 (2)	−0.0705 (3)	0.6356 (2)	5.5 (2)
C(11)	0.1659 (1)	0.3836 (2)	0.6381 (1)	3.6 (1)
C(12)	0.2909 (1)	0.1844 (2)	0.6473 (1)	2.91 (9)
C(13)	0.3198 (1)	0.1192 (2)	0.6990 (1)	3.5 (1)
C(14)	0.3919 (1)	0.1278 (2)	0.7145 (1)	4.1 (1)
C(15)	0.4342 (1)	0.1985 (3)	0.6780 (1)	4.3 (1)
C(16)	0.4056 (1)	0.2618 (3)	0.6264 (1)	4.6 (1)
C(17)	0.3333 (1)	0.2557 (2)	0.6108 (1)	3.7 (1)
C(18)	−0.0448 (1)	0.2459 (2)	0.6149 (1)	3.02 (9)
C(19)	−0.0942 (1)	0.3425 (2)	0.6209 (1)	3.7 (1)
C(20)	−0.1627 (1)	0.3284 (3)	0.5964 (1)	4.5 (1)
C(21)	−0.1832 (1)	0.2177 (3)	0.5669 (1)	4.5 (1)
C(22)	−0.1353 (1)	0.1216 (3)	0.5603 (1)	4.2 (1)
C(23)	−0.0657 (1)	0.1361 (2)	0.5837 (1)	3.5 (1)
C(24)	0.1394 (2)	0.5097 (3)	0.5464 (1)	5.7 (1)
C(25)	0.0797 (2)	0.5898 (4)	0.5596 (2)	9.7 (3)
H(1)	0.027 (1)	0.047 (2)	0.675 (1)	4.6 (6)
H(2)	0.103 (1)	−0.042 (3)	0.756 (1)	6.0 (7)
H(3)	0.178 (1)	0.116 (3)	0.807 (1)	7.7 (8)
H(4)	0.222 (1)	0.271 (2)	0.742 (1)	4.6 (6)
H(5)	0.144 (1)	0.322 (2)	0.748 (1)	4.9 (6)
H(7)	0.071 (2)	−0.079 (3)	0.595 (1)	7.2 (9)
H(8)	0.148 (2)	−0.082 (3)	0.637 (1)	7.8 (9)
H(9)	0.290 (1)	0.071 (2)	0.725 (1)	5.2 (6)
H(10)	0.409 (1)	0.083 (2)	0.750 (1)	4.6 (6)
H(11)	0.483 (1)	0.203 (2)	0.687 (1)	5.5 (6)
H(12)	0.432 (1)	0.312 (2)	0.600 (1)	4.3 (5)
H(13)	0.313 (1)	0.300 (2)	0.576 (1)	3.8 (3)
H(14)	−0.079 (1)	0.419 (2)	0.642 (1)	4.8 (6)
H(15)	−0.197 (1)	0.396 (2)	0.604 (1)	5.3 (6)
H(16)	−0.231 (1)	0.211 (2)	0.552 (1)	5.0 (6)
H(17)	−0.149 (1)	0.047 (3)	0.541 (1)	5.4 (6)
H(18)	−0.035 (1)	0.067 (2)	0.579 (1)	4.3 (6)
H(19)	0.1377	0.4943	0.5012	6.9
H(20)	0.1822	0.5547	0.5568	6.9
H(21)	0.0733	0.6569	0.5298	10.7
H(22)	0.0368	0.5393	0.5573	10.7
H(23)	0.0863	0.6242	0.6001	10.7

Table 3. Positional Parameters and B_{eq} for **5b**

Atom	x	y	z	B_{eq}
S(1)	0.37898 (8)	0.18084 (7)	0.12761 (6)	4.62 (5)
O(1)	0.6094 (2)	0.1441 (2)	0.2830 (1)	4.3 (1)
O(2)	0.3740 (2)	0.2087 (2)	0.3431 (1)	4.9 (1)
O(3)	0.5599 (2)	−0.1323 (2)	0.2356 (2)	6.8 (2)
O(4)	0.5051 (2)	−0.0270 (2)	0.3835 (1)	6.1 (1)
O(5)	0.3680 (2)	−0.1447 (2)	0.3646 (1)	5.2 (1)
N(1)	0.3052 (2)	0.0661 (2)	0.2904 (1)	3.5 (1)
C(1)	0.3896 (3)	0.1358 (2)	0.3074 (2)	3.7 (2)
C(2)	0.5117 (3)	0.1052 (2)	0.2710 (2)	3.4 (2)
C(3)	0.4767 (3)	0.0195 (2)	0.2173 (2)	3.4 (1)
C(4)	0.4286 (3)	0.0557 (2)	0.1317 (2)	3.7 (2)
C(5)	0.3260 (3)	−0.0015 (3)	0.0930 (2)	4.6 (2)
C(6)	0.2608 (3)	−0.0642 (3)	0.1300 (2)	4.6 (2)
C(7)	0.2804 (3)	−0.0884 (3)	0.2168 (2)	4.2 (2)
C(8)	0.3666 (3)	−0.0223 (2)	0.2647 (2)	3.5 (2)
C(9)	0.5798 (3)	−0.0544 (2)	0.2091 (2)	4.2 (2)
C(10)	0.4228 (3)	−0.0655 (3)	0.3440 (2)	4.5 (2)
C(11)	0.1766 (3)	0.0725 (2)	0.3096 (2)	3.7 (2)
C(12)	0.1022 (3)	0.1375 (3)	0.2691 (2)	4.6 (2)
C(13)	−0.0220 (4)	0.1456 (3)	0.2861 (3)	5.8 (2)
C(14)	−0.0712 (4)	0.0897 (4)	0.3425 (3)	6.5 (3)
C(15)	0.0027 (4)	0.0257 (4)	0.3835 (3)	6.4 (3)
C(16)	0.1281 (4)	0.0166 (3)	0.3676 (3)	5.2 (2)
C(17)	0.5109 (3)	0.2363 (2)	0.0883 (2)	4.0 (2)
C(18)	0.5371 (4)	0.2244 (3)	0.0080 (2)	5.2 (2)
C(19)	0.6400 (5)	0.2665 (4)	−0.0217 (3)	6.5 (3)
C(20)	0.7176 (5)	0.3197 (4)	0.0271 (4)	7.0 (3)
C(21)	0.6925 (5)	0.3331 (4)	0.1057 (4)	7.0 (3)
C(22)	0.5891 (4)	0.2916 (3)	0.1371 (3)	5.5 (2)
C(23)	0.6979 (3)	−0.0351 (3)	0.1695 (2)	3.9 (2)
C(24)	0.7342 (3)	0.0520 (3)	0.1432 (2)	4.3 (2)
C(25)	0.8470 (4)	0.0641 (4)	0.1083 (2)	5.2 (2)
C(26)	0.9253 (4)	−0.0113 (4)	0.1011 (3)	6.3 (3)
C(27)	0.8923 (4)	−0.0984 (4)	0.1278 (3)	6.7 (3)
C(28)	0.7784 (4)	−0.1108 (3)	0.1606 (2)	5.4 (2)
C(29)	0.4111 (5)	−0.1880 (4)	0.4413 (3)	7.2 (3)
C(30)	0.3422 (6)	−0.1541 (4)	0.5063 (3)	8.9 (3)
H(1)	0.498 (3)	0.054 (2)	0.097 (2)	4.1 (7)
H(2)	0.308 (3)	0.008 (2)	0.037 (2)	5.0 (8)
H(3)	0.200 (3)	−0.101 (2)	0.100 (2)	4.5 (8)
H(4)	0.315 (3)	−0.149 (2)	0.221 (2)	4.2 (8)
H(5)	0.203 (3)	−0.094 (2)	0.245 (2)	4.5 (8)
H(6)	0.138 (3)	0.173 (2)	0.228 (2)	4.7 (9)
H(7)	−0.069 (3)	0.190 (3)	0.260 (2)	6 (1)
H(8)	−0.163 (4)	0.094 (3)	0.351 (2)	8 (1)
H(9)	0.027 (4)	−0.012 (3)	0.426 (2)	7 (1)
H(10)	0.180 (3)	−0.027 (2)	0.396 (2)	4.1 (8)
H(11)	0.479 (3)	0.189 (2)	−0.023 (2)	5 (1)
H(12)	0.661 (3)	0.255 (3)	−0.078 (3)	7 (1)
H(13)	0.789 (4)	0.349 (3)	0.005 (2)	8 (1)
H(14)	0.740 (4)	0.371 (3)	0.140 (2)	7 (1)
H(15)	0.569 (3)	0.299 (2)	0.189 (2)	3.9 (8)
H(16)	0.683 (3)	0.102 (2)	0.147 (2)	4.0 (8)
H(17)	0.872 (3)	0.125 (3)	0.093 (2)	6 (1)
H(18)	1.004 (3)	−0.004 (2)	0.080 (2)	5.3 (9)
H(19)	0.945 (4)	−0.150 (3)	0.125 (3)	9 (1)
H(20)	0.749 (3)	−0.169 (2)	0.179 (2)	5 (1)
H(21)	0.425 (4)	−0.262 (3)	0.442 (2)	8 (1)
H(22)	0.503 (4)	−0.197 (3)	0.449 (2)	7 (1)
H(23)	0.3474	−0.0897	0.5150	10.5
H(24)	0.2523	−0.1697	0.4950	10.5
H(25)	0.3639	−0.1866	0.5571	10.5

yield after 1 h. This hetero D–A reaction occurred even at −60 °C to give the same adduct **17** (60%). Cyclohexa-1,3-diene, on heating at 120 °C for 4 h, gave the hetero D–A adduct **18** in 90% yield. The Claisen rearrangement of the adduct **17** was prohibited, and on heating at 200 °C for 90 h, no rearrangement product was formed, but instead the 4-quinolone **16** (13%), a pyrolyzate of **1**, was generated. This prohibition of the rearrangement is attributable to the steric hindrance in this rigid ring system. On the other hand, the Claisen rearrangement of **18** at 200 °C for 30 h gave the hydroindole **19** in 34% yield. Direct D–A reaction, if it occurred, should give the stereoisomer **20** (*endo* addition product).

In conclusion, the thermal cycloaddition reaction of the benzoyl-dioxopyrroline **1** with 1,3-dienes proceeds competitively *via* two types of D–A reaction, a normal and a

hetero D–A pathway. Both types of D–A reaction are stereo- and regioselective.

In the normal D–A pathway the electron-deficient double bond of the dioxopyrroline ring acts as a dienophile and the diene acts as an enophile, as in most D–A reactions. However, in the hetero D–A pathway, where the electronic demand is reversed, the enone of the 4-benzoyl and the double bond of the dioxopyrroline ring act as an electron-deficient diene (enophile) and the electron-rich 1,3-diene acts as a dienophile. When the 1,3-diene is sufficiently electron-rich, the D–A reaction proceeds in a normal manner, and otherwise it operates predominantly in a hetero manner. In particular, when the normal D–A pathway is sterically hindered, the hetero D–A operates exclusively.

Interestingly, pyrolysis of the hetero D–A adducts, unless sterically prohibited, results in Claisen rearrangement in a stereoselective manner to give the stereoisomer of the normal D–A adduct.

Experimental

Unless otherwise stated, the following procedures were adopted. All melting points were taken on a Yanagimoto micro hot-stage melting point apparatus (Yanagimoto MP type) and are uncorrected. IR spectra were measured with a JASCO FT/IR-5000 as KBr disks or Nujol mulls and values are given in cm^{-1}. UV spectra were measured with a Hitachi U-3200 spectro-photometer in dioxane and values are given in λ_{max} nm (ε). NMR spectra were taken on a JEOL JNM-α500 (^1H, 500 MHz; ^{13}C, 125 MHz), a JNM-GX270 (^1H, 270 MHz, ^{13}C, 67.5 MHz), or an EX-90 (^1H, 90 MHz; ^{13}C, 22.5 MHz) NMR spectrometer in $CDCl_3$ solution using tetramethylsilane (TMS) as an internal standard. The chemical shifts are given in δ values. Low-resolution-mass spectra (LRMS) and high-resolution mass spectra (HRMS) were determined on a JEOL JMS-HX110A spectrometer at 30 eV with a direct inlet system. Elemental analyses were recorded on a Yanaco CHN-corder MT-3. For column chromatography, silica gel (Mallinkrodt type 150A or Wako-gel C-200) was used. Thin layer chromatography (TLC) was performed on Merck precoated Silica gel 60 F_{254} plates.

Cycloaddition Reaction of 1 with Butadiene A solution of **1** (2 mmol) and butadiene (5 ml) in toluene (25 ml) was heated in a sealed tube under the conditions described in Table 1. After removal of the solvent *in vacuo*, the residue in CH_2Cl_2–benzene was purified by silica gel column chromatography. Elution with benzene–CH_2Cl_2 and crystallization of the product from CH_2Cl_2–Et_2O gave **4a**. Further elution with CH_2Cl_2 and crystallization of the product from CH_2Cl_2–Et_2O gave **3a**, in the yields shown in Table 1.

(3*R**,4a*R**)-4a-Ethoxycarbonyl-4,4a,6,7-tetrahydro-6,7-dioxo-1,5-diphenyl-3-vinyl-5*H*-pyrano[4,3-*b*]pyrrole (**3a**): Yellow prisms, mp 247—248 °C. IR (Nujol): 1740, 1730, 1600. UV: 320 (15800). ^1H-NMR: 1.29 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.83 (1H, t, J=13 Hz, H-4), 2.92 (1H, dd, J=13, 3 Hz, H-4), 4.30 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 5.21—5.25 (1H, m, H-3), 5.40 (1H, d, J=11 Hz, $CH=C\underline{H}_2$), 5.55 (1H, d, J=17 Hz, $CH=C\underline{H}_2$), 6.01 (1H, ddd, J=17, 11, 6 Hz, $C\underline{H}=CH_2$), 7.26—7.28 (2H, m, Ph), 7.34—7.37 (1H, m, Ph), 7.43—7.49 (4H, m, Ph), 7.54—7.58 (1H, m, Ph), 7.88—7.90 (2H, m, Ph). ^{13}C-NMR: 14.0 ($COOCH_2\underline{C}H_3$), 33.8 (C4), 61.8 (C3), 63.1 ($COO\underline{C}H_2CH_3$), 77.4 (C4a), 104.6 (C7a), 119.0 ($CH=\underline{C}H_2$), 125.2 (2C, Ph), 127.7 (2C, Ph), 128.2 (Ph), 129.6 (2C, Ph), 130.0 (2C, Ph), 130.8 (Ph), 132.5 (Ph), 134.6 ($\underline{C}H=CH_2$), 135.0 (Ph), 162.5 (C6), 164.9 ($\underline{C}OOCH_2CH_3$), 170.7 (C1), 177.9 (C7). *Anal.* Calcd for $C_{24}H_{21}NO_5$: C, 71.44; H, 5.26; N, 3.47. Found: C, 71.21; H, 5.23; N, 3.34.

(3a*S**,7a*R**)-3a-Benzoyl-7a-ethoxycarbonyl-3a,4,7,7a-tetrahydro-1-phenyl-1*H*-indole-2,3-dione (**4a**): Colorless prisms, mp 150—152 °C. IR (Nujol): 1780, 1740, 1715, 1640, 1600. UV: 245 (19300), 340 (1900). ^1H-NMR: 1.24 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 2.51 (1H, dd, J=19, 5 Hz, H-4), 2.83 (1H, ddd, J=19, 3, 2 Hz, H-7), 3.00 (1H, dt, J=3, 19 Hz, H-4), 3.14 (1H, dt, J=2, 19 Hz, H-7), 4.28 (2H, qd, J=7, 2 Hz, $COOC\underline{H}_2CH_3$), 5.63—5.67 (1H, m, H-5 or H-6), 5.72—5.76 (1H, m, H-5 or H-6), 7.07—7.09 (2H, m, Ph), 7.40—7.47 (3H, m, Ph), 7.52 (2H, dd, J=8, 7 Hz, Ph), 7.62 (1H, dd, J=8, 7 Hz, Ph), 8.11 (1H, d, J=9 Hz, Ph), 8.11 (1H, d, J=7 Hz, Ph). ^{13}C-NMR: 13.8 ($COOCH_2\underline{C}H_3$), 24.2 (C7), 30.2 (C4), 63.1 ($COO\underline{C}H_2CH_3$), 66.4 (C3a), 66.9 (C7a), 120.7 (C5 or C6), 124.0 (C5 or C6), 127.6 (2C, Ph), 128.5 (2C, Ph), 129.3 (Ph), 129.6 (2C, Ph), 130.9 (2C, Ph), 133.5 (Ph), 133.6 (Ph), 134.3 (Ph), 160.1 (C2), 171.7 ($\underline{C}OOCH_2CH_3$), 190.2 (COPh), 196.0 (C3). *Anal.* Calcd for $C_{24}H_{21}NO_5$: C, 71.44; H, 5.26; N, 3.47. Found: C, 71.46; H, 5.29; N, 3.30.

Thermal Rearrangement of 3a A solution of **3a** (100 mg) in toluene (10 ml) was heated in a sealed tube at 160 °C for 8 h. After removal of the solvent *in vacuo*, the residue was crystallized from CH_2Cl_2–Et_2O to give **4a** (83 mg, 83%).

Cycloaddition Reaction of 1 with (*E*)-Pentadiene A solution of **1** (698 mg, 2 mmol) and (*E*)-pentadiene (680 mg, 10 mmol) in toluene (25 ml) was heated in a sealed tube at 100 °C for 6 h. After removal of the solvent *in vacuo*, the residue was recrystallized from CH_2Cl_2–Et_2O to give **3b** (126 mg, 15%) as yellow prisms. The mother liquor from **3b** was concentrated *in vacuo*, and the residue was chromatographed over silica gel. Elution with benzene–CH_2Cl_2 and crystallization of the product from CH_2Cl_2–Et_2O gave **4b** (698 mg, 69%) as colorless prisms.

(3*R**,4a*R**)-4a-Ethoxycarbonyl-4,4a,6,7-tetrahydro-6,7-dioxo-1,5-diphenyl-3-(*E*)-1′-propenyl-5*H*-pyrano[4,3-*b*]pyrrole (**3b**): mp 202—205 °C. IR (KBr): 1727, 1711. UV: 234 (10600), 323 (11900). ^1H-NMR: 1.29 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.79 (3H, dd, J=16.5, 1.5 Hz, $C\underline{H}_3$),1.82 (1H, dd, J=13, 12 Hz, H-4), 2.88 (1H, dd, J=13, 3 Hz, H-4), 4.29 (2H, qd, J=7, 0.6 Hz, $COOC\underline{H}_2CH_3$), 5.18 (1H, m, H-3), 5.63 (1H, ddq, J=15, 7, 1.5 Hz, $C\underline{H}=CH$), 5.99 (1H, dq, J=15, 6.5 Hz, $CH=C\underline{H}$), 7.26—7.28 (2H, m, Ph), 7.33—7.37 (1H, m, Ph), 7.42—7.49 (4H, m, Ph), 7.53—7.57 (1H, m, Ph), 7.86—7.89 (2H, m, Ph). ^{13}C-NMR: 14.1 ($COOCH_2\underline{C}H_3$), 17.9 ($\underline{C}H_3$), 34.2 (C4), 61.9 (C4a), 63.1 ($COO\underline{C}H_2CH_3$), 78.0 (C3), 104.5 (C7a), 125.2 (2C, Ph), 127.7 (2C, Ph), 127.8 ($\underline{C}H=CH$), 128.1 (Ph), 129.6 (2C, Ph), 130.0 (2C, Ph), 131.0 (Ph), 132.1 ($CH=\underline{C}H$), 132.5 (Ph), 135.1 (Ph), 162.6 (C6), 165.3 ($\underline{C}OOCH_2CH_3$), 170.8 (C1), 177.9 (C7). *Anal.* Calcd for $C_{25}H_{23}NO_5$: C, 71.93; H, 5.55; N, 3.36. Found: C, 71.71; H, 5.67; N, 3.36.

(3a*S**,4*S**,7a*R**)-3a-Benzoyl-7a-ethoxycarbonyl-3a,4,7,7a-tetrahydro-4-methyl-1-phenyl-1*H*-indole-2,3-dione (**4b**): mp 140—143 °C. IR (KBr): 1775, 1754, 1725, 1665, 1599. UV: 253 (14100). ^1H-NMR: 1.14 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.35 (3H, d, J=7 Hz, $C\underline{H}_3$), 2.60 (1H, dd, J=18, 6 Hz, H-7), 2.98 (1H, ddd, J=18, 5, 3 Hz, H-7), 3.33 (1H, m, H-4), 4.13 (1H, dq, J=11, 7 Hz, $COOC\underline{H}_2CH_3$), 4.20 (1H, dq, J=11, 7 Hz, $COOC\underline{H}_2CH_3$), 5.68 (1H, dt, J=9, 3 Hz, H-5), 5.81 (1H, tt, J=9, 3 Hz, H-6), 7.13 (2H, m, Ph), 7.4—7.5 (5H, m, Ph), 7.59 (1H, t, J=7 Hz, Ph), 7.86 (2H, d, J=7 Hz, Ph). ^{13}C-NMR: 13.5 ($COOCH_2\underline{C}H_3$), 17.0 ($\underline{C}H_3$), 26.2 (C7), 38.6 (C4), 62.9 ($COO\underline{C}H_2CH_3$), 69.3 (C3a), 70.3 (C7a), 123.6 (C5 or C6), 127.1 (2C, Ph), 128.1 (2C, Ph), 129.2 (C5 or C6), 129.6 (2C, Ph), 130.0 (2C, Ph), 130.4 (Ph), 133.1 (Ph), 133.9 (Ph), 135.0 (Ph), 160.4 (C2), 171.1 ($\underline{C}OOCH_2CH_3$), 193.8 (COPh), 198.1 (C3). *Anal.* Calcd for $C_{25}H_{23}NO_5$: C, 71.93; H, 5.55; N, 3.36. Found: C, 71.67; H, 5.61; N, 3.30.

Cycloaddition Reaction of 1 with (*Z*)-Pentadiene A solution of **1** (698 mg, 2 mmol) and (*Z*)-pentadiene (680 mg, 10 mmol) in toluene (25 ml) was heated in a sealed tube at 100 °C for 24 h. After removal of the solvent *in vacuo*, the residue was crystallized from CH_2Cl_2–Et_2O to give (3*R**,4a*R**)-4a-ethoxycarbonyl-4,4a,6,7-tetrahydro-6,7-dioxo-1,5-diphenyl-3-(*Z*)-1′-propenyl-5*H*-pyrano[4,3-*b*]pyrrole (**3c**) as yellow prisms, mp 263—267 °C, 608 mg (73%). IR (KBr): 1725, 1707. UV: 324 (11900), 235 (10300). ^1H-NMR: 1.30 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.79 (3H, dd, J=7, 1.5 Hz, $C\underline{H}_3$), 1.83 (1H, dd, J=13, 12 Hz, H-4), 2.80 (1H, dd, J=13, 3 Hz, H-4), 4.30 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 5.56—5.63 (2H, m, H-3 and $C\underline{H}=CH$), 5.86 (1H, ddd, J=14, 9.5, 7 Hz, $CH=C\underline{H}$), 7.27—7.29 (2H, m, Ph), 7.32—7.37 (1H, m, Ph), 7.43—7.51 (4H, m, Ph), 7.53—7.57 (1H, m, Ph), 7.86—7.89 (2H, m, Ph). ^{13}C-NMR: 13.6 ($\underline{C}H_3$), 14.1 ($COOCH_2\underline{C}H_3$), 33.8 (C4), 61.9 (C4a), 63.1 ($COO\underline{C}H_2CH_3$), 73.2 (C3), 104.4 (C7a), 125.3 (2C, Ph), 127.1 ($\underline{C}H=CH$), 127.7 (2C, Ph), 128.2 (Ph), 129.6 (2C, Ph), 130.0 (2C, Ph), 130.9 (Ph), 131.1 ($CH=\underline{C}H$), 132.5 (Ph), 135.0 (Ph), 162.7 (C6), 165.5 ($\underline{C}OOCH_2CH_3$), 170.9 (C1), 177.9 (C7). *Anal.* Calcd for $C_{25}H_{23}NO_5$: C, 71.93; H, 5.55; N, 3.36. Found: C, 71.73; H, 5.63; N, 3.37.

Thermal Rearrangement of 3b A toluene (5 ml) solution of **3b** (25 mg) was heated in a sealed tube at 100 °C for 15 h. After removal of the solvent *in vacuo*, the residue was purified by short silica gel column chromatography (eluting with CH_2Cl_2) to give (3a*S**,4*R**,7a*R**)-3a-benzoyl-7a-ethoxycarbonyl-3a,4,7,7a-tetrahydro-4-methyl-1-phenyl-

1*H*-indole-2,3-dione (**15**) as a colorless gum, 20 mg (80%). IR (KBr): 1773, 1734, 1665. UV: 250 (12900). ^{1}H-NMR: 1.11 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.15 (3H, d, J=8 Hz, $C\underline{H}_3$), 2.49 (1H, dd, J=19, 5 Hz, H-7), 2.80—2.86 (1H, m, H-4), 3.19 (1H, dq, J=19, 3 Hz, H-7), 4.07 (1H, dq, J=11, 7 Hz, $COC\underline{H}_2CH_3$), 4.14 (1H, dq, J=11, 7 Hz, $COC\underline{H}_2CH_3$), 5.65—5.70 (1H, m, H-5), 5.79—5.85 (1H, m, H-6), 7.08—7.10 (2H, m, Ph), 7.41—7.50 (5H, m, Ph), 7.55 (1H, t, J=7 Hz, Ph), 7.81 (2H, d, J=8 Hz, Ph). ^{13}C-NMR: 13.7 ($COOCH_2\underline{C}H_3$), 16.3 ($\underline{C}H_3$), 26.2 (C7), 36.0 (C4), 63.5 ($COO\underline{C}H_2CH_3$), 66.0 (C3a), 69.2 (C7a), 123.3 (C5), 127.6 (2C, Ph), 127.9 (2C, Ph), 129.4 (C6), 129.4 (2C, Ph), 129.7 (2C, Ph), 129.7 (Ph), 132.5 (Ph), 133.8 (Ph), 138.7 (Ph), 160.4 (C2), 171.9 ($\underline{C}OOCH_2CH_3$), 190.8 (COPh), 198.6 (C3). HRMS Calcd for $C_{25}H_{23}NO_5$ (M^+): 417.1576: Found 417.1601.

Thermal Rearrangement of 3c 1) A xylene (10 ml) solution of **3c** (117 mg) was heated in a sealed tube at 300 °C for 65 h. After removal of the solvent *in vacuo*, the residue was purified by PTLC with CH_2Cl_2–MeOH (1%), to give a 1 : 4 mixture of **4b** and **15** (the ratio was calculated from ^{1}H-NMR data) (44 mg, 38%), and **3c** (44 mg, 38%).

2) A xylene (10 ml) solution of **3c** (134 mg) was heated in a sealed tube at 300 °C for 90 h. After removal of the solvent *in vacuo*, the residue was purified by silica gel column chromatography. Elution with benzene–CH_2Cl_2 gave the 1 : 2 mixture of **4b** and **15** (the ratio was calculated from ^{1}H-NMR data) (38 mg, 28%). Subsequent elution with MeOH gave **16** (47 mg, 46%).

Cycloaddition Reaction of 1 with 1-Substituted Butadienes (General Procedure) A solution of **1** (698 mg, 2 mmol) and 1-substituted butadiene (10 mmol) in toluene (25 ml) was heated in a sealed tube under the conditions shown in Table 1. After removal of the solvent *in vacuo*, the residue was crystallized from CH_2Cl_2–Et_2O to give **5** in the yields shown in Table 1.

(3a*S**,4*R**,7a*R**)-3a-Benzoyl-7a-ethoxycarbonyl-3a,4,7,7a-tetrahydro-4-trimethylsilyloxy-1-phenyl-1*H*-indole-2,3-dione (**5a**): Colorless prisms, mp 149—151 °C. IR (Nujol): 1790, 1745, 1660, 1600. UV: 255 (16600). ^{1}H-NMR: 0.19 (9H, s, OTMS), 1.21 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 2.64 (1H, dd, J=20, 4 Hz, H-7), 2.97 (1H, dd, J=20, 2 Hz, H-7), 4.26 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 5.12 (1H, br s, H-4), 5.70—5.76 (2H, m, H-5 and H-6), 7.10—7.12 (2H, m, Ph), 7.37—7.45 (3H, m, Ph), 7.56 (2H, t, J=8 Hz, Ph), 7.65 (1H, t, J=7 Hz, Ph), 8.23 (1H, d, J=9 Hz, Ph), 8.24 (1H, d, J=7 Hz, Ph). ^{13}C-NMR: 0.25 (OTMS), 13.8 ($COOCH_2\underline{H}H_3$), 24.4 (C7), 62.9 ($COO\underline{C}H_2CH_3$), 65.7 (C3a), 69.9 (C4), 72.8 (C7a), 125.2 (C5 or C6), 125.5 (C5 or C6), 127.3 (2C, Ph), 128.4 (2C, Ph), 128.8 (Ph), 129.5 (2C, Ph), 131.0 (2C, Ph), 133.9 (Ph), 133.9 (Ph), 134.3 (Ph), 160.7 (C2), 171.6 ($\underline{C}OOCH_2CH_3$), 190.0 (COPh), 195.0 (C3). *Anal.* Calcd for $C_{27}H_{29}NO_6Si$: C, 65.95; H, 5.96; N, 2.85. Found: C, 65.82; H, 5.91; N, 3.05.

(3a*S**,4*R**,7a*R**)-3a-Benzoyl-7a-ethoxycarbonyl-3a,4,7,7a-tetrahydro-1-phenyl-4-thiophenyl-1*H*-indole-2,3-dione (**5b**): Colorless prisms, mp 185—187 °C. IR (Nujol): 1780, 1730, 1660, 1600. UV: 252 (17000), 290 sh (4600). ^{1}H-NMR: 1.21 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 2.61 (1H, dd, J=20, 5 Hz, H-7), 3.12, (1H, ddd, J=20, 6, 3 Hz, H-7), 4.26 (2H, ddq, J=22, 11, 7 Hz, $COOC\underline{H}_2CH_3$), 4.62 (1H, m, H-4), 5.73—5.76 (1H, m, H-5 or H-6), 5.96—6.00 (1H, m, H-5 or H-6), 7.16—7.21 (4H, m, Ph), 7.39—7.49 (7H, m, Ph), 7.54—7.56 (2H, m, Ph), 7.76 (1H, td, J=10 Hz, Ph), 7.76 (1H, d, J=7 Hz, Ph). ^{13}C-NMR: 13.8 ($COOCH_2\underline{C}H_3$), 24.1 (C7), 49.6 (C4), 63.2 ($COO\underline{C}H_2CH_3$), 66.4 (C3a), 69.6 (C7a), 123.4 (C5 or C6), 124.7 (C5 or C6), 127.5 (2C, Ph), 128.3 (2C, Ph), 129.1 (2C, Ph), 129.6 (2C, Ph), 129.64 (2C, Ph), 131.1 (2C, Ph), 133.5 (Ph), 133.7 (Ph), 133.8 (2C, Ph), 134.7 (Ph), 160.8 (C2), 171.6 ($\underline{C}OOCH_2CH_3$), 187.7 (COPh), 195.0 (C3). *Anal.* Calcd for $C_{30}H_{25}NO_5S$: C, 70.42; H, 4.94; N, 2.74. Found: C, 70.25; H, 4.92; N, 2.66.

(3a*S**,4*R**,7a*R**)-4-Acetoxy-3a-benzoyl-7a-ethoxycarbonyl-3a,4,7,7a-tetrahydro-1-phenyl-1*H*-indole-2,3-dione (**5c**): Colorless prisms, mp 257—259 °C. IR (Nujol): 1781, 1760, 1740, 1670, 1600. UV: 256 (15200), 290 sh (3600). ^{1}H-NMR: 1.24 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 2.15 (3H, s, $OCOC\underline{H}_3$), 2.69 (1H, ddd, J=20, 5, 1.5 Hz, H-7), 3.07 (1H, ddd, J=20, 5, 2.5 Hz, H-7), 4.29 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 5.73—5.77 (1H, m, H-5 or H-6), 5.91—5.95 (1H, m, H-5 or H-6), 6.30 (1H, d, J=4 Hz, H-4), 7.10—7.12 (2H, m, Ph), 7.41—7.48 (3H, m, Ph), 7.52—7.56 (2H, m, Ph), 7.63—7.67 (1H, m, Ph), 8.10—8.12 (2H, m, Ph). ^{13}C-NMR: 14.0 ($COOCH_2\underline{C}H_3$), 20.9 ($OCOC\underline{H}_3$), 24.6 (C7), 63.5 ($COO\underline{C}H_2CH_3$), 66.4 (C3a), 68.6 (C4), 70.9 (C7a), 121.6 (C5 or C6), 127.6 (2C, Ph), 128.1 (C5 or C6), 128.8 (2C, Ph), 129.4 (Ph), 129.8 (2C, Ph), 131.2 (2C, Ph), 133.7 (Ph), 133.8 (Ph), 134.5 (Ph), 160.7 (C2), 169.3 ($O\underline{C}OCH_3$), 171.7 ($\underline{C}OOCH_2CH_3$), 189.1 (COPh), 194.0 (C3). *Anal.* Calcd for $C_{26}H_{23}NO_7$: C, 67.66; H, 5.03; N, 3.04. Found: C, 67.31; H, 4.99; N, 2.96.

Cycloaddition Reaction of 1 with Isoprene A solution of **1** (698 mg, 2 mmol) and isoprene (680 mg, 10 mmol) in toluene (25 ml) was heated in a sealed tube at 100 °C for 18 h. After removal of the solvent *in vacuo*, the residue was chromatographed over silica gel. Elution with benzene–CH_2Cl_2 and crystallization of the product from CH_2Cl_2–Et_2O gave **9** (561 mg, 67%) as colorless prisms. Further elution with CH_2Cl_2 gave a mixture of **7** and **8**, which was separated by PTLC with CH_2Cl_2–MeOH (1%), and crystallized from CH_2Cl_2–Et_2O to give **7** (57 mg, 7%) and **8** (119 mg, 14%).

(3*R**,4a*R**)-4a-Ethoxycarbonyl-4,4a,6,7-tetrahydro-3-methyl-6,7-dioxo-1,5-diphenyl-3-vinyl-5*H*-pyrano[4,3-*b*]pyrrole (**7**): Yellow prisms, mp 212-214 °C. IR (KBr): 1729, 1657, 1651, 1638, 1593. UV: 321 (12400), 235 (12500). ^{1}H-NMR: 1.19 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.64 (3H, s, $C\underline{H}_3$), 2.07 (1H, d, J=13 Hz, H-4), 3.09 (1H, d, J=13 Hz, H-4), 4.10 (2H, qd, J=11, 7 Hz, $COOC\underline{H}_2CH_3$), 4.95 (1H, d, J=11 Hz, $CH=C\underline{H}_2$), 4.96 (1H, d, J=17 Hz, $CH=C\underline{H}_2$), 5.69 (1H, dd, J=11, 17 Hz, $C\underline{H}$=CH2), 7.17—1.19 (2H, m, Ph), 7.39—7.42 (1H, m, Ph), 7.44—8.47 (2H, m, Ph), 7.50—7.52 (2H, m, Ph), 7.55—7.59 (1H, m, Ph), 7.91—7.93 (2H, m, Ph). ^{13}C-NMR: 14.0 ($COOCH_2\underline{C}H_3$), 29.0 ($\underline{C}H_3$), 38.4 (C4), 62.3 (C4a), 62.6 ($COO\underline{C}H_2CH_3$), 81.1 (C3), 105.4 (C7a), 113.1 ($CH=\underline{C}H_2$), 127.4 (2C, Ph), 127.7 (2C, Ph), 128.9 (Ph), 130.8 (Ph), 132.3 (Ph), 134.7 (Ph), 139.2 ($\underline{C}H=CH_2$), 162.7 (C6), 163.8 (C1), 168.7 ($\underline{C}OOCH_2CH_3$), 178.2 (C7). *Anal.* Calcd for $C_{25}H_{23}NO_5$: C, 71.93; H, 5.55; N, 3.36. Found: C, 71.63 H, 5.55; N, 3.44.

(3*R**,4a*R**)-4a-Ethoxycarbonyl-4,4a,6,7-tetrahydro-3-isopropenyl-6,7-dioxo-1,5-diphenyl-5*H*-pyrano[4,3-*b*]pyrrole (**8**): Yellow prisms, mp 228—231 °C. IR (KBr): 1729, 1591. UV: 321 (13200), 233 (12400). ^{1}H-NMR: 1.29 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.90 (1H, dd, J=12, 13 Hz, H-4), 1.91 (3H, s, $C\underline{H}_3$), 2.88 (1H, dd, J=3, 13 Hz, H-4), 4.30 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 5.12 (1H, s, $CH=C\underline{H}$), 5.20 (1H, dd, J=3, 12 Hz, H-3), 5.23 (1H, s, $CH=C\underline{H}$), 7.27—7.29 (2H, m, Ph), 7.34—7.38 (1H, m, Ph), 7.44—7.52 (5H, m, Ph), 7.88—7.90 (2H, m, Ph). ^{13}C-NMR: 14.1 ($COOCH_2\underline{C}H_3$), 17.8 ($\underline{C}H_3$), 32.5 (C4), 61.9 (C4a), 63.1 ($COO\underline{C}H_2CH_3$), 80.0 (C3), 104.6 (C7a), 115.1 ($\underline{C}H=CH$), 125.2 (2C, Ph), 127.8 (2C, Ph), 128.2 (Ph), 129.6 (2C, Ph), 129.9 (2C, Ph), 130.9 (Ph), 132.6 (Ph), 135.0 (Ph), 141.4 ($\underline{C}H=CH$), 162.6 (C6), 165.2 (C1), 170.7 ($\underline{C}OOCH_2CH_3$), 177.9 (C7). HRMS Calcd for $C_{25}H_{23}NO_5$ (M^+): 417.1573. Found: 417.1537.

(3a*S**,7a*R**)-3a-Benzoyl-7a-ethoxycarbonyl-3a,4,7,7a-tetrahydro-6-methyl-1-phenyl-1*H*-indole-2,3-dione (**9**): Colorless prisms, mp 169—171 °C. IR (KBr): 1775, 1736, 1661, 1599. UV: 253 (16700). ^{1}H-NMR: 1.24 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.59 (3H, br s, CH_3), 2.31 (1H, d, J=9 Hz, H-7), 2.83 (1H, dt, J=19, 2 Hz, H-4), 2.93 (1H, dd, J=19, 1 Hz, H-7), 3.13 (1H, dt, J=2, 19 Hz, H-4), 4.29 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 5.32—5.33 (1H, m, H-5), 7.03—7.05 (2H, m, Ph), 7.42—7.47 (3H, m, Ph), 7.50—7.53 (2H, m, Ph), 7.60—7.63 (1H, m, Ph), 8.11—8.13 (2H, m, Ph). ^{13}C-NMR: 13.9 ($COOCH_2\underline{C}H_3$), 22.9 ($\underline{C}H_3$), 28.8 (C7), 30.5 (C4), 63.1 ($COO\underline{C}H_2CH_3$), 66.1 (C3a), 67.7 (C7a), 114.5 (C5), 127.6 (2C, Ph), 128.4 (2C, Ph), 129.3 (Ph), 129.6 (2C, Ph), 131.0 (2C, Ph), 131.6 (C6), 133.4 (Ph), 133.6 (Ph), 134.2 (Ph), 160.0 (C2), 171.8 ($\underline{C}OOCH_2CH_3$), 190.2 (COPh), 196.0 (C3). *Anal.* Calcd for $C_{25}H_{23}NO_5$: C, 71.93; H, 5.55; N, 3.36. Found: C, 71.69; H, 5.66; N, 3.36.

Thermal Rearrangement of 7 A solution of **7** (18 mg) in toluene (5 ml) was heated in a sealed tube at 160 °C for 12 h. After removal of the solvent *in vacuo*, the residue was purified by PTLC with CH_2Cl_2–MeOH (1%) and crystallized from CH_2Cl_2–Et_2O to give **9** (11mg, 62%).

Thermal Rearrangement of 8 A solution of **8** (34 mg) in toluene (5 ml) was heated in a sealed tube at 160 °C for 8 h. After removal of the solvent *in vacuo*, the residue was purified by short silica gel column chromatography (eluting with CH_2Cl_2) to give (3a*S**,7a*R**)-3a-benzoyl-7a-ethoxycarbonyl-3a,4,7,7a-tetrahydro-5-methyl-1-phenyl-1*H*-indole-2,3-dione (**14**) as colorless prisms, mp 145—146 °C, 28 mg (82%). IR (KBr): 1775, 1740, 1661, 1599. UV: 253 (15700). ^{1}H-NMR: 1.21 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.65 (3H, s, CH_3), 2.48 (1H, ddd, J=19, 7, 5 Hz, H-7), 2.72 (1H, dd J=19, 3 Hz, H-7), 2.95 (2H, d, J=18 Hz, H-4), 4.25 (2H, qd, J=7, 1.5 Hz, $COOC\underline{H}_2CH_3$), 5.42—5.43 (1H, m, H-6), 7.06—7.08 (2H, m, Ph), 7.42—7.47 (3H, m, Ph), 7.51—7.54 (2H, m, Ph), 7.60—7.64 (1H, m, Ph). ^{13}C-NMR: 13.8 ($COOCH_2\underline{C}H_3$), 22.5 ($\underline{C}H_3$), 24.9 (C4), 35.0 (C7), 63.1 ($COO\underline{C}H_2CH_3$), 67.0 (C3a), 67.4 (C7a), 118.1 (C6), 127.6 (2C, Ph), 128.5 (2C, Ph), 128.9 (C5), 129.3 (Ph), 129.6 (3C, Ph), 130.8 (2C, Ph), 133.6 (Ph), 134.4 (Ph), 160.1 (C2), 171.6 ($\underline{C}OOCH_2CH_3$), 190.8

(COPh), 196.1 (C3). HRMS Calcd for $C_{25}H_{23}NO_5$ (M^+): 417.1573. Found: 417.1452.

Cycloaddition Reaction of 1 with 2-Trimethylsilyloxy-1,3-butadiene A solution of **1** (698 mg, 2 mmol) and 2-trimethylsilyloxy-1,3-butadiene (1.42 g, 10 mmol) in benzene (10 ml) was heated in a sealed tube at 100 °C for 40 min. After removal of the solvent *in vacuo*, the residue was crystallized from CH_2Cl_2–Et_2O and filtered to give **11** (396 mg, 40%) as colorless prisms. The filtrate was evaporated *in vacuo*, and the residue was chromatographed over silica gel. Elution with benzene–CH_2Cl_2 and crystallization of the product from CH_2Cl_2–Et_2O gave **12** (120 mg, 14%) as colorless prisms. Further elution with CH_2Cl_2–MeOH (1%) and crystallization from CH_2Cl_2–Et_2O–hexane gave **10** (200 mg, 24%) as colorless prisms.

(5*R**)-4-Benzoyl-5-ethoxycarbonyl-1,5-dihydro-3-hydroxy-5-(2-oxo-3-butenyl)-1-phenyl-2*H*-pyrrol-2-one (**10**): mp 168—173 °C. IR (KBr): 3110, 1748, 1698, 1676, 1640, 1599. UV: 267 (12100), 294 (11500). ^{1}H-NMR: 1.29 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 3.22 (1H, d, J=24 Hz, H-1′), 3.69 (1H, d, J=24 Hz, H-1′), 4.32 (2H, qq, J=11, 7 Hz, $COOC\underline{H}_2CH_3$), 5.66 (1H, dd, J=7.5, 4 Hz, H-3′), 6.08 (1H, d, J=4 Hz, H-4′), 6.10 (1H, d, J=7.5 Hz, H-4′), 7.15—7.60 (8H, m, Ph), 7.80—7.91 (2H, m, Ph). ^{13}C-NMR: 14.0 ($COOCH_2\underline{C}H_3$), 36.8 (C1′), 62.8 ($COO\underline{C}H_2CH_3$), 69.1 (C1), 118.7 (C5), 126.5 (2C, Ph), 128.2 (2C, Ph), 128.5 (C3′), 129.3 (C4′), 129.3 (2C, Ph), 129.5 (2C, Ph), 133.0 (Ph), 134.1 (Ph), 136.6 (Ph), 137.5 (Ph), 150.3 (C4), 166.6 (C3), 169.1 ($\underline{C}OOCH_2CH_3$), 189.7 (COPh), 196.1 (C2′). *Anal.* Calcd for $C_{24}H_{21}NO_6$: C, 68.72; H, 5.05; N, 3.34. Found: C, 68.63; H, 5.00; N, 3.46.

(3a*S**,7a*R**)-3a-Benzoyl-7a-ethoxycarbonyl-3a,4,7,7a-terahydro-6-trimethylsilyloxy-1-phenyl-1*H*-indole-2,3-dione (**11**): mp 184—186 °C. IR (KBr): 1775, 1740, 1711, 1684, 1665, 1599. UV: 251 (17000). ^{1}H-NMR: 0.10 (9H, s, OTMS), 1.24 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 2.44 (1H, d, J=19 Hz, H-7), 2.88—2.93 (1H, m, H-4), 3.06—3.14 (1H, m, H-4), 3.12 (1H, d, J=19 Hz, H-7), 4.58 (2H, qq, J=11, 7 Hz, $COOC\underline{H}_2CH_3$), 4.66—4.68 (1H, m, H-5), 7.10—7.12 (2H, m, Ph), 7.41—7.48 (3H, m, Ph), 7.50—7.53 (2H, m, Ph), 7.60—7.63 (1H, m, Ph), 8.11—8.13 (2H, m, Ph). ^{13}C-NMR: 0.1 (OTMS), 13.8 ($COOCH_2\underline{C}H_3$), 29.3 (C7), 29.4 (C4), 63.3 ($COO\underline{C}H_2CH_3$), 66.9 (C3a), 68.9 (C7a), 96.6 (C5), 127.6 (2C, Ph), 128.5 (2C, Ph), 129.3 (Ph), 129.7 (2C, Ph), 131.6 (2C, Ph), 133.4 (Ph), 133.5 (Ph), 134.5 (Ph), 148.4 (C6), 159.7 (C2), 171.5 ($\underline{C}OOCH_2CH_3$), 190.2 (COPh), 196.1 (C3). *Anal.* Calcd for $C_{27}H_{29}NO_6Si$: C, 65.97; H, 5.95; N, 2.85. Found: C, 66.07; H, 5.81; N, 2.90.

(3a*S**,7a*R**)-3a-Benzoyl-7a-ethoxycarbonyl-3a,4,7,7a-tetrahydro-1-phenyl-1*H*-indole-2,3,6-trione (**12**): mp 165—166 °C. IR (KBr): 1775, 1734, 1671, 1599. UV: 254 (15500).^{1}H-NMR: 1.21 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 2.33 (1H, ddd, J=16, 11.5, 5 Hz, H-4), 2.40 (1H, dtd, J=16, 5.5, 1 Hz, H-4), 2.68 (1H, ddd, J=15, 11.5, 5 Hz, H-5), 2.90 (1H, ddd, J=15, 5.5, 5 Hz, H-5), 2.97 (1H, dd, J=17, 1 Hz, H-7), 3.36 (1H, d, J=17 Hz, H-7), 4.25 (2H, qq, J=11, 7 Hz, $COOC\underline{H}_2CH_3$), 7.03—7.06 (2H, m, Ph), 7.44—7.51 (3H, m, Ph), 7.54—7.57 (2H, m, Ph), 7.65—7.69 (1H, m, Ph), 8.17—8.20 (2H, m, Ph). ^{13}C-NMR: 13.8 ($COOCH_2\underline{C}H_3$), 30.7 (C4), 35.6 (C5), 41.0 (C7), 63.7 ($COO\underline{C}H_2CH_3$), 67.7 (C3a), 71.1 (C7a), 127.6 (2C, Ph), 128.7 (2C, Ph), 129.8 (Ph), 130.0 (2C, Ph), 130.7 (2C, Ph), 133.0 (Ph), 134.1 (Ph), 134.2 (Ph), 159.2 (C2), 170.6 ($\underline{C}OOCH_2CH_3$), 190.4 (COPh), 196.3 (C3), 204.4 (C6). *Anal.* Calcd for $C_{24}H_{21}NO_6$: C, 68.72; H, 5.05; N, 3.34. Found: C, 68.62; H, 5.21; N, 3.34.

Hydrolysis of 11 A solution of **11** (110 mg) in THF (10 ml) was stirred with concentrated HCl (3 drops) overnight. After dilution with CH_2Cl_2, the reaction mixture was washed with water, dried over Na_2SO_4 and evaporated. The residue was crystallized from CH_2Cl_2–Et_2O to give **12** (87 mg, 92%).

Cycloaddition Reaction of 1 with Cyclopentadiene 1) A solution of **1** (698 mg, 2 mmol) and cyclopentadiene (700 mg, 10 mmol) in benzene (25 ml) was stirred at room temperature for 1 h. After removal of the solvent *in vacuo*, the crystalline residue was crystallized from CH_2Cl_2–Et_2O to give (5a*S**,8a*R**,8b*R**)-8b-ethoxycarbonyl-2,3,8a,8b-tetrahydro-2,3-dioxo-1,4-diphenyl-1*H*-cyclopenta[1′,2′ : 5,6]pyrano[4,3-*b*]-pyrrol-6-ene (**17**) as yellow prisms, mp 193—194.5 °C, 740 mg (89%). IR (KBr): 1730, 1710, 1610, 1600. UV: 233 (10200), 265 sh (4550), 340 (11300). ^{1}H-NMR: 1.25 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 2.08 (1H, ddd, J=17.5, 8, 1 Hz, H-8), 2.18 (1H, ddd, J=17.5, 4, 2 Hz, H-8), 3.79 (1H, dd, J=15.5, 8 Hz, H-8a), 4.31 (2H, qq, J=11, 7 Hz, $COOC\underline{H}_2CH_3$), 5.86 (1H, dt, J=8, 2 Hz, H-5a), 6.05—6.09 (2H, m, H-6 and H-7), 7.30—7.33 (1H, m, Ph), 7.38—7.40 (2H, m, Ph), 7.43—7.48 (4H, m, Ph), 7.55—7.58 (1H, m, Ph), 7.87—7.90 (2H, m, Ph). ^{13}C-NMR: 13.9 ($COOCH_2\underline{C}H_3$), 33.9 (C8a), 62.9 ($COO\underline{C}H_2CH_3$), 64.3 (C8b), 88.2 (C5a), 103.9 (C3a), 123.0 (2C, Ph), 127.3 (C6 or C7), 128.0 (2C, Ph), 129.5 (2C, Ph), 129.6 (C6 or C7), 130.2 (2C, Ph), 131.3 (Ph), 133.1 (Ph), 135.5 (Ph), 138.0 (Ph), 162.4 (C2), 168.6 ($\underline{C}OOCH_2CH_3$), 170.7 (C4), 177.5 (C3). *Anal.* Calcd for $C_{25}H_{21}NO_5$: C, 72.27; H, 5.11; N, 3.37. Found: C, 72.27; H, 5.10; N, 3.31.

2) A solution of **1** (500 mg, 1.43 mmol) and cyclopentadiene (3 g, 42.8 mmol) in CH_2Cl_2 (15 ml) was stirred at −60 °C for 15 h. After removal of the solvent *in vacuo*, the crystalline residue was crystallized from CH_2Cl_2–Et_2O to give **17** (380 mg, 60%).

Cycloaddition Reaction of 1 with Cyclohexadiene A solution of **1** (698 mg, 2 mmol) and cyclohexadiene (800 mg, 10 mmol) in toluene (10 ml) was heated in a sealed tube at 120 °C for 4 h. After removal of the solvent *in vacuo*, the residue was recrystallized from CH_2Cl_2–Et_2O to give (5a*S**,9a*R**,9b*R**)-9b-ethoxycarbonyl-2,3,9a,9b-tetrahydro-2,3-dioxo-1,4-diphenyl-1*H*-cyclohexa[1′,2′ : 5,6]-pyrano[4,3-*b*]pyrrol-6-ene (**18**) as yellow prisms, mp 107—110 °C, 773 mg (90%). IR (KBr): 1727, 1657. UV: 231 (10600), 264 sh (6700), 328 (10900). ^{1}H-NMR: 1.08—1.20 (1H, m, $C\underline{H}_2$), 1.23 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$) 1.47—1.52 (1H, m, $C\underline{H}_2$), 1.85—1.99 (1H, m, $C\underline{H}_2$), 2.19 (1H, dt, J=19, 5 Hz, $C\underline{H}_2$), 2.90 (1H, ddd J=13.5, 4, 3 Hz, H-9a), 4.28 (2H, qq, J=11, 7 Hz, $COOC\underline{H}_2CH_3$), 5.41 (1H, t, J=4 Hz, H-5a), 6.06—6.19 (2H, m, H-7 and H-8), 7.27—7.41 (1H, m, Ph), 7.42—7.58 (7H, m, Ph), 7.84—7.88 (2H, m, Ph). ^{13}C-NMR: 13.8 ($COOCH_2\underline{C}H_3$), 16.8 ($\underline{C}H_2$), 24.7 ($\underline{C}H_2$), 33.5 (C9a), 62.8 ($COO\underline{C}H_2CH_3$), 64.3 (C9b), 73.0 (C5a), 101.5 (C3a), 122.3 (2C, Ph), 123.0 (C6 or C7), 126.9 (Ph), 127.6 (2C, Ph), 128.1 (C6 or C7), 129.3 (Ph), 129.7 (2C, Ph), 130.8 (Ph), 132.3 (Ph), 134.3 (Ph), 135.5 (Ph), 162.8 (C2), 164.1 ($\underline{C}OOCH_2CH_3$), 171.2 (C4), 177.5 (C3). HRMS (FAB) Calcd for $C_{26}H_{23}NO_5$ (M^++1): 430.1654. Found: 430.1654.

Thermal Rearrangement of 17 A solution of **17** (50 mg) in toluene was heated in a sealed tube at 180 °C for 24 h. After removal of the solvent *in vacuo*, the residue was crystallized from CH_2Cl_2–Et_2O to give the starting material **17** (40 mg, 80%). The mother liquor was concentrated *in vacuo*, and the residue was crystallized from CH_2Cl_2–Et_2O to give **16** (5 mg, 13%).

Thermal Rearrangement of 18 A solution of **18** (100 mg) in toluene (5 ml) was heated in a sealed tube at 200 °C for 30 h. After removal of the solvent *in vacuo*, the residue was purified by silica gel column chromatography (eluting with benzene–CH_2Cl_2) and crystallized from CH_2Cl_2–Et_2O to give **19** (34 mg, 34%). Further elution with CH_2Cl_2 gave the starting material **18** (49 mg, 49%).

(3a*S**,4*S**,7*R**,7a*R**)-3a-Benzoyl-7a-ethoxycarbonyl-3a,4,7,7a-tetrahydro-1-phenyl-4,7-ethano-1*H*-indole-2,3-dione (**19**): Colorless prisms, mp 161—162 °C. IR (KBr): 1756, 1723, 1694, 1597. UV: 244 (13100). ^{1}H-NMR: 0.89 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.30 (1H, tdd, J=13, 5, 3 Hz, H-8 or H-9), 1.41 (1H, tt, J=13, 4 Hz, H-8 or H-9), 1.64 (1H, ddt, J=13, 10, 3 Hz, H-8 or H-9), 1.82 (1H, dddd, J=14, 9.5, 5, 2 Hz, H-8 or H-9), 3.34—3.37 (1H, m, H-4 or H-7), 3.41—3.43 (1H, m, H-4 or H-7), 3.84 (1H, dq, J=11, 7 Hz, $COOC\underline{H}_2CH_3$), 3.96 (1H, dq, J=11, 7 Hz, $COOC\underline{H}_2CH_3$), 6.45 (1H, t, J=7 Hz, H-5 or H-6), 6.54 (1H, t, J=7 Hz, H-5 or H-6), 7.35—7.37 (2H, m, Ph), 7.39—7.45 (3H, m, Ph), 7.48—7.52 (3H, m, Ph), 7.55—7.57 (2H, m, Ph). ^{13}C-NMR: 13.4 ($COOCH_2\underline{C}H_3$), 18.3 (C8 or C9), 21.4 (C8 or C9), 35.7 (C4 or C7), 40.5 (C4 or C7), 62.5 ($COO\underline{C}H_2CH_3$), 68.9 (C3a), 76.7 (C7a), 126.0 (2C, Ph), 128.2 (2C, Ph), 129.0 (2C, Ph), 129.1 (Ph), 129.7 (2C, Ph), 130.7 (C5 or C6), 132.3 (Ph), 133.7 (C5 or C6), 135.2 (Ph), 137.1 (Ph), 158.8 (C2), 168.9 ($\underline{C}OOCH_2CH_3$), 196.9 (C3), 197.9 (PhCO). *Anal.* Calcd for $C_{26}H_{23}NO_5$: C, 72.71; H, 5.40; N, 3.26. Found: C, 72.65; H, 5.31; N, 3.37.

X-Ray Crystallographic Analysis The reflection data were collected on a Rigaku AFC-5 four-circle diffractometer controlled by the MSC/AFC program package, using graphite-monochromated Mo/K_α radiation with the ω–2θ scan technique to a maximum 2θ of 55° at a scan speed of 6°/min. The numbers of unique reflections collected were 5128 for **4b** and 6026 for **5b**. The structures were solved by the direct method[4] using the TEXSAN crystallographic software package. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined isotropically or placed at the calculated positions. The final cycle of full-matrix least-squares refinement was performed using the reflections with $I > 3.0\delta(I)$ (2894 for **4b** and 2469 for **5b**).

Crystal data of **4b**: colorless prisms, mp 140—143 °C: $C_{25}H_{23}NO_5$. M_r=417.46, monoclinic, a=18.866(2), b=10.526(3), c=21.421(2) Å, β=93.57(1)°, V=4246(1) Å^3, D_c=1.306 g/cm^3, Z=8. Space group, $C2/c$; crystal size, 0.3×0.4×0.4 mm. R=0.044.

Crystal data of **5b**: Colorless prisms, mp 185—187 °C: $C_{30}H_{25}NO_5$. $M_r = 511.59$, monoclinic, $a = 10.730(8)$, $b = 14.232(6)$, $c = 16.572(4)$ Å, $\beta = 93.33(3)°$, $V = 2526(2)$ Å^3, $D_c = 1.345$ g/cm^3, $Z = 4$. Space group, $P2_1/n$; crystal size, $0.3 \times 0.3 \times 0.4$ mm. $R = 0.042$.

References

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