Construction of Fused Cyclooctanoid Ring Systems via Seven-Membered Ring Carbonyl Ylides

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A series of α-diazo carbonyl compounds tethered to cyclopentanone/cyclohexanone/1-tetralone units have been synthesized using a diazomethane solution to construct various fused cyclooctane ring systems via rhodium-generated carbonyl ylides. The reaction of rhodium(II) acetate dimer with various α-diazo carbonyl compounds generated transient cyclic seven-membered ring carbonyl ylides, which underwent facile 1,3-dipolar cycloadditions with dipolarophiles, like *N*-phenylmaleimide, *p*-benzoquinone, and DMAD to furnish a variety of fused epoxy-bridged cyclooctane ring systems in a tandem manner. Interestingly, an oxepine ring system was generated via an intramolecular proton transfer of a seven-membered ring carbonyl ylide. A tri-oxa polycyclic compound was obtained in the case of *p*-benzoquinone as dipolarophile. A single-crystal X-ray analysis of a fused cyclootanoid derivative is reported to decisively establish the structure and stereochemistry of the fused epoxy-bridged cyclooctane ring systems; a further analysis revealed the existence of a unique intermolecular C–H$\cdots\pi$ interaction motif in the solid-state architecture.

Although there are many synthetic processes which involve both cyclization and cycloaddition approaches to five- and six-membered ring systems, seven- and eight-membered ring systems have not attracted much attention. Cyclization strategies to obtain medium-sized rings are often regarded as inappropriate because of entropy factors that hamper ring closure.[1] Some very imaginative and elegant cycloaddition, annulation approaches, and metal-mediated synthesis towards medium-sized rings have proven to be useful.[2–6] Additionally, ring expansion from more readily available carbocycles can provide efficient access to seven- and eight-membered rings.[6–10] Recently, a protocol for eight- and nine-membered ring synthesis using an annulation strategy has been reported[11] by Molander et al. The eight-membered ring is the latest entrant into the marked collection of carbocyclic rings present in natural products, primarily among terpenoids. In the past few years, the number of carbocyclic skeletons in which a cyclooctane forms a part of the condensed or bridged polycyclic system has proliferated rapidly. The isolation and characterization of many complex natural products containing cyclooctane rings and the attention to synthesize them in a regio-, stereo-, and enantioselective manner is an important intention in organic synthesis. Many protocols involving diverse cycloadditions, cyclizations, radical-mediated ring expansions, fragmentation methods, rearrangement methods, and coupling reactions involving eight-membered ring formations have been reported and reviewed.[12] The cyclooctane structural units present in a wide range of natural products exist either as isolated rings, or form parts of bicyclic or tricyclic frameworks, for example, tremulenediol A (**1**),[10] dumortenol (**2**),[13] and roseadione (**3**)[14] (Chart 1). A possible retro-synthetic analysis to fused cyclooctane skeletons via α-diazo ketone involving a seven-membered carbonyl ylide is shown in Scheme 1.

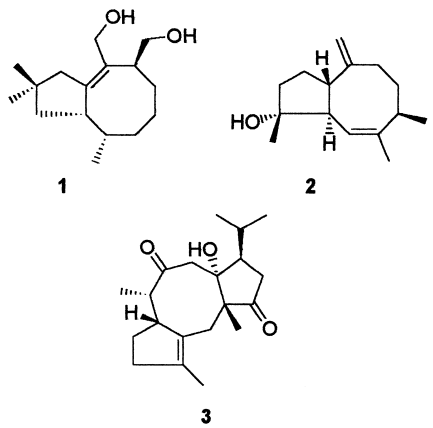
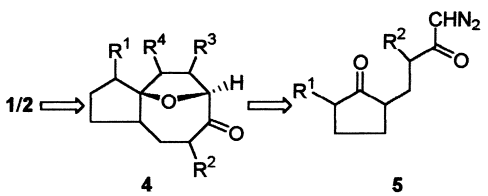


Chart 1.



Scheme 1.

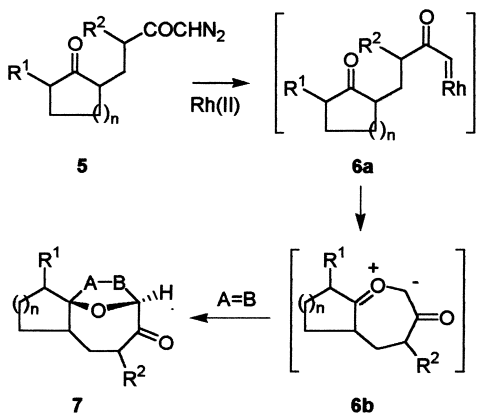
Diazo compounds have found numerous applications in organic synthesis, and their use in either carbocyclic or heterocyclic ring formation is well precedented.[15–17] The transition metal-mediated carbon-carbon bond-forming reactions from various α-diazo ketone precursors have been utilized in various natural product syntheses, such as brevicomin,[18] phorbol derivatives,[19,20] and zaragozic acid A.[21]

The chemistry of rhodium-generated five- and six-membered ring carbonyl ylides and their cycloaddition with a π-bond has been extensively studied.[22–24] Recently, we have reported the formation of five- and six-membered ring carbonyl ylides and their consequent cycloaddition reactions with various dipolarophiles as an approach to epoxy-bridged polycyclic systems.[25–29] However, the chemistry of seven-membered ring carbonyl ylides and their subsequent cycloadditions is still not skillfully exploited. There appears to be only one report[30] where seven-membered ring carbonyl ylide formation was observed. The generation of carbonyl ylides, and followed by a cycloaddition methodology represents a powerful tool to construct polycyclic rings, because it creates multiple bonds in a single operation with high regio- and stereocontrol of the remote substituents. As a consequence of our continuing interest in the development of tandem rhodium carbenoid reactions,[25–29] we herein report on both the generation and reactions of various seven-membered ring carbonyl ylides towards the synthesis of fused cyclooctanoid ring systems.

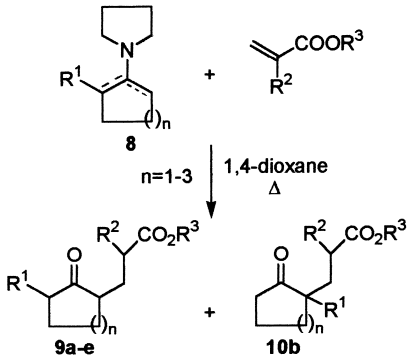
Results and Discussion

The generation of intermolecular carbonyl ylides and their subsequent 1,3-dipolar cycloaddition reactions were reported[31,32] by Huisgen and co-workers. Generation followed by cycloadditions of intramolecular carbonyl ylides have been well exploited and applied to the synthesis of epoxy-bridged cyclic systems. The epoxy-bridge serves as a latent hydroxy substituent of defined stereochemistry. Most of the studies found in the literature were carried out involving only a facile formation of intramolecular five- and six-membered ring carbonyl ylides.[15,22,23] The main feature in the generation of intramolecualr carbonyl ylides relies on an attack of the neighboring carbonyl oxygen at the rhodium carbenoid center to form a carbonyl ylide dipole, which consequently undergoes cycloaddition across a π-bond of a dipolarophile. An effective overlap could occur if the distance between rhodium carbenoid and lone pairs of carbonyl group is sufficiently close, and in turn forms an intermediate carbonyl ylide. As shown in Scheme 2, seven-membered ring carbonyl ylide intermediates **6b** are proposed to be generated in the reaction of diazo carbonyl compounds using rhodium(II) acetate as a catalyst.

To study the generation and cycloaddition behavior of seven-membered ring carbonyl ylides, the required diazo carbonyl compounds **12** were assembled from commercially available materials. The enamine,[33] prepared from corresponding cycloalkanone using pyrrolidine, was subjected to a Michael reaction with acceptors, like ethyl acrylate or methyl methacrylate, to afford the required alkylated cycloalkanone esters **9a–e**, **10b** (Scheme 3, Table 1). The reaction of enamine **8b** with ethyl acrylate afforded two products, **9b** and **10b**, due to the existence of a mixture of unsymmetrical enamines that formed from pyrrolidine and 2-methylcyclopentanone.



Scheme 2.



Scheme 3.

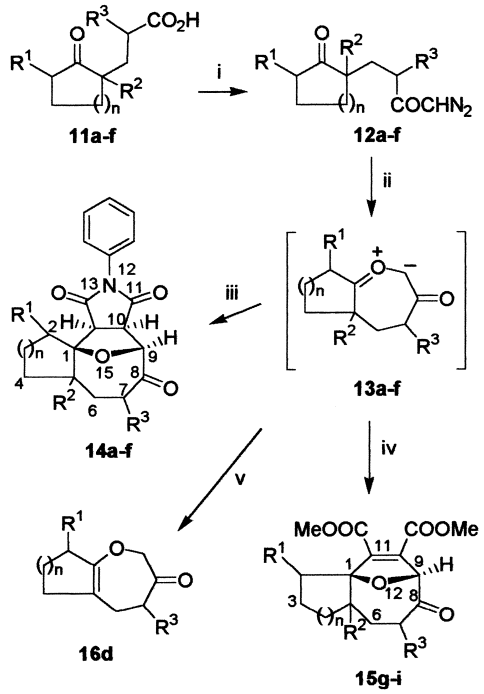
Table 1. Keto Esters **9**,**10** Produced via the Enamine Method

Product	*n*	R^1	R^2	R^3	Yield[a]/%	
					9	**10**
a	1	H	CH_3	CH_3	79	—
b	1	CH_3	H	CH_2CH_3	49	33
c	2	H	CH_3	CH_3	84	—
d	2	H	H	CH_2CH_3	76	—
e	3	H	H	CH_2CH_3	83	—

a) Yields (unoptimized) were based on cycloalkanones.

A careful hydrolysis of keto esters (prepared via Scheme 3) using 8% aqueous KOH solution afforded the corresponding acids **11a–f**, respectively, in very good yield. The treatment of acid **11a–f** with ethyl chloroformate and triethylamine resulted in a white suspension at room temperature, and the resulting mixed anhydride was treated with freshly prepared ethereal diazomethane at 0–10 °C to furnish α-diazo ketones **12a–f**, respectively (Scheme 4). To a solution of diazo ketone **12a** and *N*-phenylmaleimide in dry dichloromethane was added 0.5 mol% rhodium(II) acetate catalyst; and the reaction mixture was stirred under an argon atmosphere for 3 h at room temperature followed by chromatographic purification, which furnished exclusively product **14a** in 61% yield (Scheme 4, Table 2).

The IR spectrum of product **14a** showed characteristic strong bands at 1780 and 1717 cm^{-1} due to the presence of carbonyl groups. The ^1H NMR of product **14a** showed the characteristic singlet at δ 4.81 due to the presence of a bridgehead proton (H-9) and two doublets at δ 3.69 and 3.21 for H-10/14, respectively, with a coupling constant of J = 8.2 Hz. ^{13}C NMR and dept-135 spectra exhibited the presence of eight CH, four CH_2, one CH_3, and five quaternary carbons, that evidently confirmed the formation of product **14a**. This reaction reveals that the generation of a seven-membered ring carbonyl



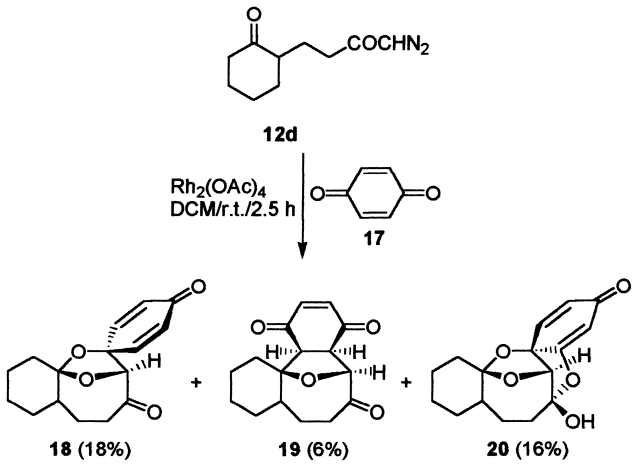
Scheme 4. Reagents: (i) a) ClCOOEt, NEt_3, Ether, b) CH_2N_2, Ether; (ii) $Rh_2(OAc)_4$, DCM; (iii) *N*-phenylmaleimide; (iv) DMAD; (v) cyclopenta-2,4-dienylidenecyclohexane.

Table 2. Fused Cyclooctanes **14**,**15** Produced via Scheme 4

Entry	*n*	R^1	R^2	R^3	Time	Yield[a]/%	
					h	**14**	**15**
a	1	H	H	CH_3	2.5	61	—
b	1	CH_3	H	H	3.0	58	—
c	1	H	CH_3	H	3.0	49	—
d	2	H	H	H	2.0	57	—
e	2	H	H	CH_3	2.5	58	—
f	3	H	H	H	3.0	64	—
g	1	H	H	CH_3	1.5	—	54
h	1	CH_3	H	H	2.5	—	61
i	1	H	CH_3	H	3.0	—	45

a) Yields (unoptimized) refer to isolated and chromatographically pure compounds of **14** and **15**.

ylide as a transient species in the presence of rhodium(II) acetate is followed by trapping with *N*-phenylmaleimide to furnish the cycloadduct **14a** containing a cyclooctane ring system. In order to generalize, we carried out a rhodium-catalyzed reaction with other diazo carbonyl compounds **12b–f** to afford respective fused cyclooctane ring systems **14b–f**. Similarly, the reaction of diazo ketones **12a–c** in the presence of DMAD also afforded the corresponding fused cyclooctane ring systems **15g–i**. All of these products were clearly characterized based on their interrelated spectral data. The reaction of diazo ketone **12d** with cyclopenta-2,4-dienylidenecyclohexane in dry dichloromethane was performed in the presence of rhodium(II) acetate, followed by chromatographic purification of the reaction mixture, which afforded a rearranged product **16d**, which was characterized as 4,5,6,7,8,9-hexahydrobenzo[*b*]oxepin-3-one (**16d**) without forming the expected cycloaddition product. This reaction indicated that seven-membered carbonyl ylide **13d** did not undergo cycloaddition with the electron-rich fulvene (Scheme 4). It is interesting to note that we have very recently demonstrated the cycloaddition reaction of five-membered ring carbonyl ylides with various electron-rich fulvenes.[29]

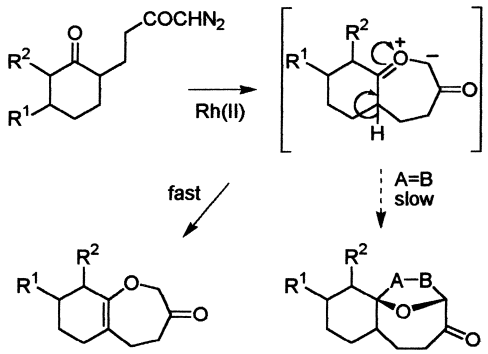


Scheme 5.

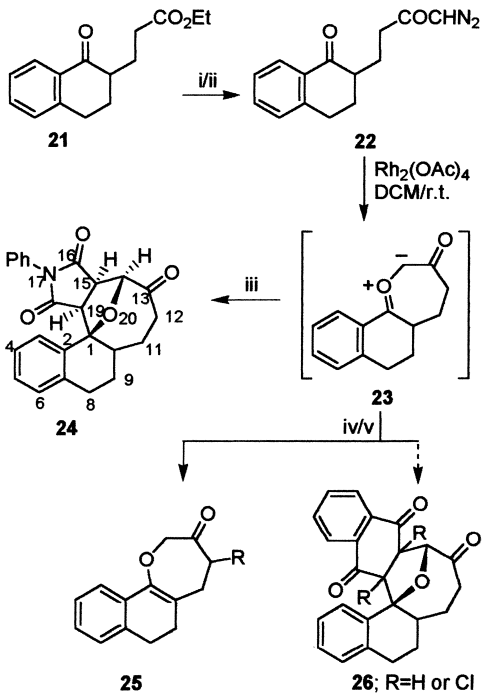
Consequently, we performed a rhodium-catalyzed reaction of diazo ketone **12d** in the presence of *p*-benzoquinone (**17**) as a bifunctional dipolarophile (Scheme 5). This reaction was carried out in the presence of 0.5 mol% of rhodium(II) acetate in dry dichloromethane, and allowed to be stirred at room temperature; the reaction was followed by TLC until disappearance of diazo ketone **12d**. The reaction mixture was purified through neutral alumina column chromatography to afford three products **18–20**. All of these products were characterized based on their interrelated spectral data. The reaction furnished C=O (**18**), C=C (**19**), and C=O/water (**20**) addition products in a similar manner to five- and six-membered ring carbonyl ylide reactions[28] with *p*-benzoquinone as a dipolarophile. The formation of product **20** may be due to the addition of a water molecule on **18**, followed by a Michael-type cyclization reaction under the performed experimental condition. It may be noted that product **20** was produced in a single step from diazo carbonyl compound **12d** by forming four new C–O bonds and one C–C bond, in turn producing five chiral centers in the molecule.

The reaction of diazo ketone **12d** was performed in the absence of any dipolarophiles under similar reaction conditions, followed by column purification of the reaction mixture, which furnished product **16d** in 69% yield (Scheme 4). The formation of product **16d** may be attributed to an intramolecular proton transfer to produce 4,5,6,7,8,9-hexahydrobenzo[*b*]oxepin-3-one. A general mechanism for a fast proton transfer is shown in Scheme 6.[34]

After studying various ring systems, we were interested in further illustrating the scope and synthetic utility of the tandem cyclization-cycloaddition sequence using seven-membered ring carbonyl ylides. To this end, we opted to study the rhodium-catalyzed behavior of diazo carbonyl compound **22** (Scheme 7, Table 3). We synthesized the required diazo car-



Scheme 6.



Scheme 7. Reagents: (i) 5% KOH, r.t., 5 h, 96%; (ii) a) ethyl chloroformate/triethylamine, r.t., 45 min., b) CH_2N_2, dry ether, 0 °C, 12 h then 10 °C, 2 h, 60%; (iii) *N*-phenylmaleimide, 3.5 h; (iv) 1,4-naphthoquinone, 3.5 h; (v) 2,3-dichloro-1,4-naphthoquinone, 3 h.

Table 3. Yields of Product **24**,**25** Produced via Scheme 7

Reactant	Yield[a]/%	
	24	**25**
N-Phenylmaleimide	40	13
1,4-Naphthoquinone	—	42
2,3-Dichloro-1,4-naphthoquinone	—	44
$Rh_2(OAc)_4$	—	60

a) Yields (unoptimized) were based on **22**.

bonyl compound **22**, starting from α-tetralone. The enamine[33] prepared from (α-tetralone and pyrrolidine was subjected to a Michael addition reaction with ethyl acrylate in dry 1,4-dioxane to furnish 3-(1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)propionic acid ethyl ester (**21**). Upon the hydrolysis of **21**, the corresponding acid was obtained, which was subsequently

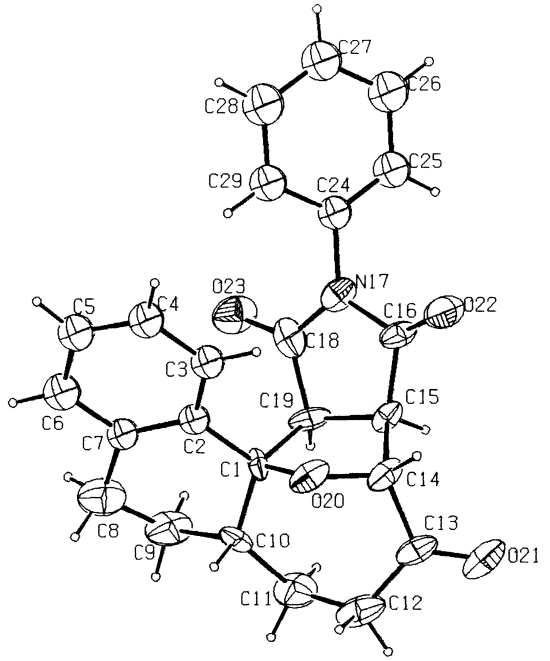


Fig. 1. ORTEP view of tetralone derived cyclooctanoid ring system **24**.

treated with ethyl chloroformate in the presence of triethylamine to afford a mixed anhydride, which upon a treatment with diazomethane furnished diazo compound **22**. A rhodium(II)-catalyzed reaction of diazo ketone **22** was performed with various dipolarophiles, like naphthoquinones and *N*-phenylmaleimide. In the presence of *N*-phenylmaleimide, the reaction afforded cycloadduct **24** and proton-transfer product 4,5,6,7-tetrahydronaphtho[1,2-*b*]-[1]oxepin-3(2*H*)-one (**25**), which were well characterized based on interrelated spectral data.

The IR spectrum of product **24** showed characteristic peaks at 1782 and 1716 cm^{-1} due to the presence of carbonyl groups. The ^1H NMR spectrum revealed the characteristic singlet at δ 4.98 for the presence of a bridgehead proton, two doublets at δ 4.04 and 3.47 for H-15/19 protons with coupling constants of J = 8.4 Hz, respectively. The ^{13}C NMR and dept-135 spectra exhibited the presence of eleven CH, four CH_2, and seven quaternary carbons. All of these spectral analyses evidently confirmed the formation of a novel cyclooctane derivative. To determine the stereochemical aspects, product **24** was further characterized by a single-crystal X-ray analysis (Fig. 1), which clearly revealed the formation of an *exo* cycloadduct. The observed angle of the epoxy-bridge was 110.2° (C14–O20–C1). The cell parameters and intensity of the compound were measured in the range θ = 2-22.5° at room temperature. Twenty-five reflections with θ = 7–10° were used to obtain accurate cell dimensions. Three standard reflections, monitored every 1 h, showed no significant crystal decay for the entire period of data collection. The crystal orientation, cell refinement, and intensity measurements were carried out using the program CAD-4PC. The raw intensity data were corrected for Lorentz polarization effects. The Lorentz polarization correction and data reduction were carried out using the NRCVAX program.[35] Because the number of reflections to the parameter ratio was

low, the phenyl rings in the molecule were kept isotropic in the final refinement cycles using the program SHELXL-97 until convergence was reached. All of these the H-atoms were fixed stereochemically by a riding model using the program SHELXL-97.[36] The final cycles of a least-squares refinement in the locked fashion described earlier yielded *R*-value of R_1 = 9.012% (wR_2 = 22.40%) for compound **24**.

Furthermore, we were eager to view the packing interactions in molecule **24**. The packing arrangement molecule **24** in its solid-state architecture revealed two novel C–H···π interactions and viewed down *a*-axis, as shown in Fig. 2. It is interesting to note that molecules are held together in the crystal lattice via C–H···π interactions.[37] The molecules are associated as dimers with the *N*-phenyl rings of the dimeric units having come closer to the aromatic part of tetralone from either end to make effective C–H···π interactions. The C–H···π parameters for this dimeric interaction are H3···C2G = 3.119 Å, C3···C2G = 3.850 Å, and < C3–H3···C2G = 136.78°, where C2G is the centroid of C24–C29.

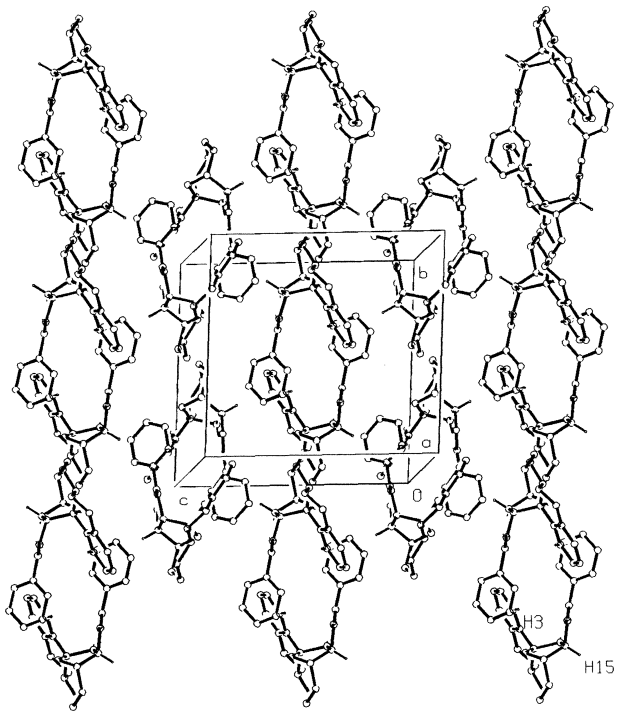


Fig. 2. Packing diagram of compound **24** viewed down *a*-axis showing the dimeric association. Only H3 and H15 hydrogen atoms, which are involved in C–H···π interactions included in the figure.

The dimers run parallel to the *b*-axis (Fig. 2). The H15 atom (*endo* proton) of the associated dimeric molecules are further involved in C–H···π bonding with the aromatic part tetralone (C2–C7) of adjacent dimeric layers from both the side extending the layers into a sheet-like supramolecular architecture. The parameters for this C–H···π interaction are H15–C1G = 2.728 Å, C15···C1G = 3.657 Å, and < C15–H15···C1G = 158.26°, where C1G is the centroid of the fused phenyl ring, C2–C7. A close-up ORTEP view of both of these C–H···π interactions is shown in Fig. 3.

Finally, the reaction of diazo ketone **22** in the presence of 0.5 mol% rhodium(II) acetate dimer was carried out with 1,4-naphthoquionone as well as 2,3-dichloro-1,4-naphthoquinone as dipolarophiles. In these cases, we isolated only the intramolecular proton-transfer product **25** (Scheme 7) instead of the respective cycloadduct **26**. The reason may be due to a favorable fast transfer of a proton[34] (Scheme 6) instead of a cycloaddition process and the strain involved in the product formation. Similarly, the reaction was carried out in the absence of any dipolarophile with rhodium(II) acetate catalyst; purification of the reaction mixture afforded the proton-transfer product in 61% yield.

In summary, we have described the generation of various seven-membered ring carbonyl ylides from various α-diazo carbonyl compounds and their subsequent 1,3-dipolar cycloaddition with dipolarophiles to afford fused cyclooctane ring systems. Interestingly, the reaction of a seven-membered carbonyl ylide with *p*-benzoquinone provided three epoxy-bridged polycyclic systems in a single step. A proton-transfer rearrangement was observed in the case of carbonyl ylides **13d**, **23** instead of undergoing cycloaddition with a dipolarophile, such as cyclopenta-2,4-dienylidenecyclohexane or 1,4-naphthoquinones, respectively. A single-crystal X-ray analysis of molecule **24** and its interactions in a solid-state architecture were carried out to evidently assign the stereochemical aspects.

Experimental

The melting points are uncorrected. The IR spectra were re-

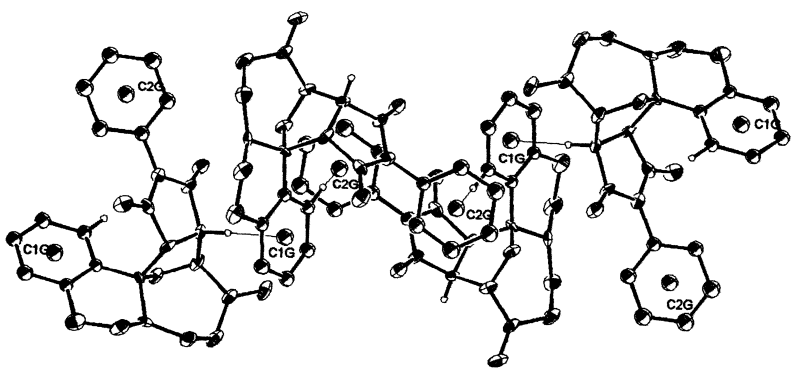


Fig. 3. ORTEP diagram of **24** showing the C–H···π interactions (thin lines) present in Fig. 2 that stabilizing the molecule in the crystal lattice. C1G and C2G are the centroid of the aromatic part of tetralone C2–C7 and *N*-phenyl ring C24 to C29, respectively.

corded on a Perkin–Elmer Spectrum GX FT-IR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance DPX 200 (200 MHz and 50.3 MHz, respectively) spectrometer and referenced to TMS. Carbon types were determined from DEPT ^{13}C NMR experiments. The chemical-shift (δ) values are reported as parts per million (ppm). The multiplicity of the ^{1}H NMR signal is designated by one of the following abbreviations: s = singlet, d = doublet, q = quartet, br = broad, and m = multiplet. Coupling constants (J) are reported in Hz. Mass analyses were performed on a Jeol D-300 (with an ionizing voltage of 70 eV) or a Jeol M Station 700 (FD^+ method in absolute dichloromethane) mass spectrometer. Elemental analyses were performed on a Perkin–Elmer Model 2400 analyzer. An X-ray crystallographic analysis was carried out in an Enraf Nonius CAD-4 diffractometer with Mo $K\alpha$ radiation. All of the reactions were carried out under an argon atmosphere and solutions dried with anhydrous magnesium sulfate. Diethyl ether was distilled from sodium benzophenone ketyl immediately before use. Toluene/Benzene were dried and stored over sodium prior to use. Dry dichloromethane was dried using P_2O_5. Thin-layer chromatography was performed on silica/alumina plates and components were visualized by observation under iodine or by sulfuric acid charring. Column chromatography was performed on silica gel/neutral alumina. Care was taken to avoid light during the course of the reaction in the synthesis of diazo compounds and their further conversion.

General Procedure for Alkylation of Enamines of Cyclic Alkanones to Prepare Cycloalkanone Esters (9, 10b, and 21) via Stork-Enamine Alkylation Method.[33] A benzene solution (100 cm^3) of appropriate cyclic alkanone (50 mmol) and pyrrolidine (100 mmol) was refluxed under a water separator in the presence of a catalytic amount of *p*-toluenesulfonic acid for 12–15 h until no water separation. The solvent, excess of pyrrolidine was removed under reduced pressure and the crude enamine was taken in dry 1,4-dioxane (100 cm^3) under an argon atmosphere. To the reaction mixture, ethyl acrylate or methyl methacrylate (65 mmol) was added at room temperature with stirring and refluxed for 12–15 h. After an appropriate period, 15 cm^3 of water was added and the reaction mixture further refluxed for 2 h. The reaction mixture was concentrated, the crude reaction mixture was extracted using ethyl acetate (3×75 cm^3), and the organic layer was separated and washed twice with dilute hydrochloric acid (50 cm^3), brine solution, dried over anhydrous $MgSO_4$, and concentrated in a vacuum. The crude residue was purified over silica-gel column chromatography to afford the respective alkylated products **9a–e**,**10b**.

Methyl-2-methyl-3-(2-oxocyclopentyl)propionate (9a). A benzene solution (50 cm^3) of cyclcopentanone (3 g, 35.7 mmol) and pyrrolidine (6.1 cm^3, 71.4 mmol) was refluxed under a water separator to obtain the pyrrolidine enamine of cyclcopentanone; to the crude enamine reaction mixture in dry 1,4-dioxane (30 cm^3) was added methyl methacrylate (5 cm^3, 46.4 mmol) at room temperature with stirring, and refluxed for 12 h; and the reaction mixture was worked-up according to the general method to obtain **9a** (5.1 g, 79%). Colorless oil; IR (neat) 2959, 2879, 1737, 1736, 1458, 1269, 1156, 1095 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.67 (3H, s, OCH_3), 2.70–2.55 (1H, m), 2.33–2.00 (6H, m), 1.85–1.49 (3H, m), 1.17 (3H, d, J = 6.8 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 220.4 (C=O), 176.3 (COO), 51.6 (OCH_3), 47.4 (CH), 38.0 (CH), 37.6 (CH_2), 33.8 (CH_2), 29.9 (CH_2), 20.7 (CH_2), 17.2 (CH_3).

Ethyl-3-(3-methyl-2-oxocyclopentyl)propionate (9b). A benzene solution (50 cm^3) of 2-methylcylcopentanone (5 g, 51 mmol) and pyrrolidine (8.5 cm^3, 102 mmol) was refluxed under a water separator to obtain the pyrrolidine enamine of 2-methylcyclopentanone; to the crude enamine reaction mixture in dry 1,4-dioxane (50 cm^3) was added ethyl acrylate (7.1 cm^3, 66.3 mmol) at room temperature with stirring, and refluxed for 13 h; and the reaction mixture was worked-up according to the general method to obtain **9b** (4.9 g, 49%) and **10b** (3.3 g, 33%). **9b**: Colorless oil; IR (neat) 2935, 1734, 1313, 1232, 1170, 1140 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 4.11 (2H, q, J = 7.2 Hz, OCH_2), 2.45–1.40 (10H, m), 1.25 (3H, t, J = 7.2 Hz, CH_2CH_3), 1.09 (3H, d, J = 6.8 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 221.2 (C=O), 172.8 (COO), 60.0 (OCH_2), 47.7 (CH), 43.9 (CH), 31.8 (CH_2), 29.6 (CH_2), 27.3 (CH_2), 25.3 (CH_2), 14.2 (CH_2), 14.0 (CH_3).

Ethyl-3-(1-methyl-2-oxocyclopentyl)propionate (10b). Colorless oil; IR (neat) 2936, 2861, 1735, 1230 1201 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 4.10 (2H, q, J = 7.2 Hz, OCH_2), 2.40–1.65 (8H, m), 1.60–1.20 (2H, m), 1.25 (3H, t, J = 7.2 Hz, CH_2CH_3), 1.02 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 221.8 (C=O), 172.9 (COO), 60.0 (OCH_2), 47.0 (quat-C), 37.1 (CH_2), 35.7 (CH_2), 31.1 (CH_2), 29.2 (CH_2), 21.1 (CH_3), 18.3 (CH_2), 14.0 (CH_3). Found: C, 66.69; H, 9.16%. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15%.

Methyl-2-methyl-3-(2-oxocyclohexyl)propionate (9c). A benzene solution (50 cm^3) of cyclohexanone (5 g, 51 mmol) and pyrrolidine (8.5 cm^3, 102 mmol) was refluxed under a water separator to obtain the pyrrolidine enamine of cyclohexanone; to the crude enamine reaction mixture in dry 1,4-dioxane (50 cm^3) was added methyl methacrylate (7.1 cm^3, 66.3 mmol) at room temperature with stirring, and refluxed for 15 h; and the reaction mixture was worked-up according to the general method to obtain **9c** (8.5 g, 84%). Colorless oil; IR (neat) 2937, 2862, 1734, 1711, 1453, 1376, 1313, 1231, 1200, 1171, 1141 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.60 (3H, s, OCH_3), 2.35–1.20 (12H, m), 1.15 (3H, d, J = 6.8 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 212.4 (C=O), 177.4 (COO), 51.2 (OCH_3), 48.1 (CH), 41.7 (CH_2), 36.6 (CH), 33.9 (CH_2), 33.2 (CH_2), 27.8 (CH_2), 24.8 (CH_2), 17.4 (CH_3).

Ethyl-3-(2-oxocyclohexyl)propionate (9d). A benzene solution (50 cm^3) of cyclohexanone (5 g, 51 mmol) and pyrrolidine (8.5 cm^3, 102 mmol) was refluxed under a water separator to obtain the pyrrolidine enamine of cyclohexanone; to the crude enamine reaction mixture in dry 1,4-dioxane (50 cm^3) was added ethyl acrylate (7.2 cm^3, 66.3 mmol) at room temperature with stirring, and refluxed for 12 h; and the reaction mixture was worked-up according to the general method to obtain **9d** (7.6 g, 76%). Colorless oil; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 4.11 (2H, q, J = 7.2 Hz, OCH_2), 2.48–2.23 (5H, m,), 2.20–1.35 (8H, m), 1.25 (3H, t, J = 7.2 Hz, CH_2CH_3); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 212.5 (C=O), 173.6 (COO), 60.2 (OCH_2), 49.8 (CH), 42.2 (CH_2), 34.2 (CH_2), 31.9 (CH_2), 28.1 (CH_2), 25.1 (CH_2), 24.9 (CH_2), 14.2 (CH_3).

Ethyl-3-(2-oxocycloheptyl)propionate (9e). A benzene solution (50 cm^3) of cycloheptanone (5 g, 44.6 mmol) and pyrrolidine (7.5 cm^3, 89.3 mmol) was refluxed under a water separator to obtain the pyrrolidine enamine of cycloheptanone; to the crude enamine reaction mixture in dry 1,4-dioxane (30 cm^3) was added ethyl acrylate (6.3 cm^3, 58 mmol) at room temperature with stirring, and refluxed for 15 h; and the reaction mixture was worked-up according to the general method to obtain **9e** (7.9 g, 83%). Colorless oil; IR (neat) 2980, 2931, 2858, 1735, 1702, 1452, 1376, 1246, 1176, 1034 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 4.13 (2H, q, J = 7.2 Hz, OCH_2), 2.55–2.20 (5H, m), 2.18–1.50 (7H, m),

1.41–1.21 (3H, m), 1.25 (3H, t, J = 7.2 Hz, CH_2CH_3); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 215.2 (C=O), 173.3 (COO), 60.2 (OCH_2), 51.1 (CH), 42.8 (CH_2), 31.9 (CH_2), 31.5 (CH_2), 29.3 (CH_2), 28.5 (CH_2), 27.2 (CH_2), 24.2 (CH_2), 14.2 (CH_3).

Ethyl-3-(1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)propionate (21). A benzene solution (50 cm^3) of 1-tetralone (5 g, 34.2 mmol) and pyrrolidine (5.7 cm^3, 68.4 mmol) was refluxed under a water separator to obtain the pyrrolidine enamine of 1-tetralone; to the crude enamine reaction mixture in dry 1,4-dioxane (50 cm^3) was added ethyl acrylate (4.9 cm^3, 45 mmol) at room temperature with stirring, and refluxed for 15 h; and the reaction mixture was worked-up according to the general method to obtain **21** (6.1 g, 73%). Pale orange oil; IR (neat) 2980, 2935, 2867, 1732, 1683, 1601, 1452, 1373, 1290, 1225, 1032 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.02–7.95 (1H, m, arom-H), 7.46–7.14 (3H, m, arom-H), 4.12 (2H, q, J = 7.1 Hz, OCH_2), 3.01–2.95 (2H, m), 2.58–2.15 (5H, m), 1.95–1.77 (3H, m), 1.24 (3H, t, J = 7.1 Hz, CH_2CH_3); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 199.4 (C=O), 173.4 (COO), 143.8 (arom quat-C), 133.2 (=CH), 132.4 (arom quat-C), 128.7 (=CH), 127.3 (=CH), 126.5 (=CH), 60.2 (OCH_2), 46.7 (CH), 31.9 (CH_2), 28.7 (CH_2), 28.6 (CH_2), 25.1 (CH_2), 14.2 (CH_3).

General Procedure for the Synthesis of Diazo Ketones (12a–f and 22), from Keto Esters. Keto ester **9a–e/10b** (12 mmol) was carefully hydrolyzed using 8% aqueous potassium hydroxide solution (20 cm^3) with stirring at room temperature. The reaction was monitored by TLC and continued until disappearance of the starting material. The reaction mixture was extracted with ether (3×10 cm^3), acidified the aqueous layer (pH = 5), and extracted with ether (3×15 cm^3). The organic phase was concentrated under reduced pressure at room temperature to obtain the corresponding keto acids **11a–f**. To a solution containing 1 equivalent of appropriate keto acid **11a–f** (10 mmol) in 100 cm^3 of freshly distilled dry ether was added 1.2 equivalent of freshly distilled ethyl chloroformate followed by the slow addition of 1.5 equivalent of dry triethylamine. The resulting mixture was stirred at room temperature for 45 min. and the solid that formed was filtered under an inert atmosphere. After the filtrate was added to 20 mmol of freshly prepared ethereal diazomethane solution, the mixture stirred under an argon atmosphere for 12 h at 0 °C; it was then allowed to warm to 10 °C for a period of 2 h under an argon atmosphere. At the end of this time, the solvent was removed under reduced pressure and chromatographic purification of this residue through a neutral alumina column (pre-washed by ethyl acetate) led to the corresponding diazo ketones **12a–f** with 15% ethyl acetate–hexane elution. The same sequences of reactions were carried out to prepare the diazo ketone **22** from the keto ester **21**.

2-(4-Diazo-2-methyl-3-oxobutyl)cyclopentanone (12a). The hydrolysis of the ester **9a** (1 g, 5.4 mmol) with an 8% aqueous potassium hydroxide solution for 6 h afforded 2-methyl-3-(2-oxocyclopentyl)propionic acid (**11a**, 0.8 g, in 88%). A solution containing 0.7 g (4.1 mmol) of crude acid in dry ether was treated with 0.47 cm^3 (4.9 mmol) of ethyl chloroformate and 0.87 cm^3 (6.2 mmol) of triethylamine to afford a mixed anhydride, and a treatment with 8.2 mmol of a diazomethane solution gave the diazo ketone **12a** (0.5 g, 62%). **11a**: Colorless thick oil; IR (neat) 3234, 2972, 2881, 1735, 1730, 1460, 1405, 1158, 1120, 1038, 737 cm^{-1}; ^{1}H NMR (CD_3CN, 200 MHz) δ 4.70 (1H, br s, COOH), 2.67–2.56 (1H, m), 2.29–1.96 (6H, m), 1.83–1.28 (3H, m), 1.16 (3H, d, J = 6.8 Hz, CH_3). **12a**: Thick yellow oil; IR (neat) 2967, 2878, 2104, 1811, 1736, 1639, 1458, 1325, 1155, 1023 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.37 (1H, br s, CHN_2), 2.84–2.74 (1H, m), 2.28–1.99 (6H, m), 1.86–1.20 (3H, m), 1.18 (3H, d, J = 6.8 Hz, CH_3). Found: C, 61.80; H, 7.29; N, 14.46%. Calcd for $C_{10}H_{14}N_2O_2$: C, 61.84; H, 7.27; N, 14.42%.

2-(4-Diazo-3-oxobutyl)-5-methylcyclopentanone (12b). The hydrolysis of the ester **9b** (2 g, 10.1 mmol) with an 8% aqueous potassium hydroxide solution for 6 h afforded 3-(3-methyl-2-oxocyclopentyl)propionic acid (**11b**, 1.5 g, in 88%). A solution containing 1.4 g (8.2 mmol) of crude acid in dry ether was treated with 1 cm^3 (10 mmol) of ethyl chloroformate and 1.8 cm^3 (12.4 mmol) of triethylamine to afford a mixed anhydride, and a treatment with 16.4 mmol of a diazomethane solution gave the diazo ketone **12b** (0.8 g, 49%). **11b**: Colorless thick oil; IR (neat) 3349, 1736, 1457, 1418, 1211, 1151, 1121 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 4.89 (1H, br s, COOH), 2.60–1.75 (7H, m), 1.70–1.39 (3H, m), 1.11 (3H, d, J = 6.8 Hz, CH_3). **12b**: Bright yellow oil; IR (neat) 3095, 2961, 2105, 1736, 1642, 1450, 1376, 1340, 1067 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.39 (1H, br s, CHN_2), 2.60–1.59 (6H, m), 1.55–1.30 (4H, m), 1.10 (3H, d, J = 6.8 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 222.2 (C=O), 194.8 (C=O), 54.8 (CHN_2), 48.1 (CH), 44.5 (CH), 41.1 (CH_2), 31.6 (CH_2), 27.3 (CH_2), 26.0 (CH_2), 14.7 (CH_3). Found: C, 61.69; H, 7.26; N, 14.45%. Calcd for $C_{10}H_{14}N_2O_2$: C, 61.84; H, 7.27; N, 14.42%.

2-(4-Diazo-3-oxobutyl)-2-methylcyclopentanone (12c). The hydrolysis of the ester **10b** (2 g, 10.1 mmol) with an 8% aqueous potassium hydroxide solution for 4.5 h afforded 3-(1-methyl-2-oxocyclopentyl)propionic acid (**11c**, 6 g, in 90%). A solution containing 1.4 g (8.2 mmol) of crude acid in dry ether was treated with 1 cm^3 (10.1 mmol) of ethyl chloroformate and 1.8 cm^3 (12.4 mmol) of triethylamine to afford a mixed anhydride, and a treatment with 16.4 mmol of a diazomethane solution gave the diazo ketone **12c** (0.8 g, 48%). **11c**: Colorless thick oil; IR (neat) 3309, 1732, 1453, 1411, 1219, 1165, 1120, 986 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.71 (1H, br s, COOH), 2.65–1.80 (7H, m), 1.75–1.45 (3H, m), 1.00 (3H, s, CH_3). **12c**: Bright yellow oil; IR (neat) 3096, 2961, 2105, 1734, 1642, 1455, 1378, 1345, 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.40 (1H, br s, CHN_2), 2.60–2.40 (4H, m), 2.35–1.40 (6H, m), 1.01 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 222.9 (C=O), 194.8 (C=O), 54.7 (CHN_2), 47.8 (quat-C), 37.8 (CH_2), 36.5 (CH_2), 30.1 (CH_2), 28.0 (CH_2), 21.7 (CH_3), 18.8 (CH_2). Found: C, 61.76; H, 7.23; N, 14.39%. Calcd for $C_{10}H_{14}N_2O_2$: C, 61.84; H, 7.27; N, 14.42%.

2-(4-Diazo-3-oxobutyl)cyclohexanone (12d).[30] The hydrolysis of the ester **9d** (3 g, 15.1 mmol) with an 8% aqueous potassium hydroxide solution for 4 h afforded 3-(2-oxocyclohexyl)propionic acid (2.3 g in 90%). A solution containing 2 g (11.8 mmol) of crude acid in dry ether was treated with 1.3 cm^3 (14.1 mmol) of ethyl chloroformate and 2.5 cm^3 (17.6 mmol) of triethylamine to afford a mixed anhydride, and a treatment with 23.5 mmol of a diazomethane solution gave the diazo ketone **12d** (1.2 g, 53%). **12d**: Thick yellow oil; IR (neat) 2934, 2861, 2075, 1712, 1709, 1648, 1448, 1291, 1265, 1219, 1167 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.31 (1H, br s, CHN_2), 2.44–2.29 (5H, m), 2.17–1.35 (8H, m); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 212.8 (C=O), 194.9 (C=O), 54.4 (CH), 49.8 (CH_2), 42.2 (CH_2), 38.4 (CH_2), 34.3 (CH_2), 28.1 (CH_2), 25.0 (CH_2), 24.7 (CH_2).

2-(4-Diazo-2-methyl-3-oxobutyl)cyclohexanone (12e). The hydrolysis of the ester **9c** (1 g, 5.1 mmol) with an 8% aqueous potassium hydroxide solution for 5 h afforded 2-methyl-3-(2-oxocyclohexyl)propionic acid (**11e**, 0.7 g, in 81%). A solution containing 0.6 g (3.3 mmol) of crude acid in dry ether was treated with 0.37 cm^3 (3.9 mmol) of ethyl chloroformate and 0.69 cm^3 (4.9

mmol) of triethylamine to afford a mixed anhydride, and a treatment with 6.6 mmol of a diazomethane solution gave the diazo ketone **12e** (0.4 g, 54%). **11e**: Colorless thick oil; IR (neat) 3180, 2937, 2864, 1706, 1653, 1456, 1339, 1235, 1124 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.71 (1H, br s, COOH), 2.60–1.27 (12H, m), 1.19 (3H, d, J = 6.8 Hz, CH_3). **12e**: Thick yellow oil; IR (neat) 2932, 2862, 2096, 1733, 1708, 1629, 1453, 1736, 1259, 1200 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 5.33 (1H, br s, CHN_2), 2.34–1.25 (12H, m), 1.17 (3H, d, J = 6.8 Hz, CH_3). Found: C, 63.39; H, 7.79; N, 13.39%. Calcd for $C_{11}H_{16}N_2O_2$: C, 63.44; H, 7.74; N, 13.45%.

2-(4-Diazo-3-oxobutyl)cycloheptanone (12f). The hydrolysis of the ester **9e** (1.5 g, 7.1 mmol) with an 8% aqueous potassium hydroxide solution for 5 h afforded 3-(2-oxocycloheptyl)propionic acid (1.2 g in 93%). A solution containing 1 g (5.4 mmol) of crude acid in dry ether was treated with 0.62 cm^3 (6.5 mmol) of ethyl chloroformate and 1.2 cm^3 (8.2 mmol) of triethylamine to afford a mixed anhydride, and a treatment with 10.8 mmol of a diazomethane solution gave the diazo ketone **12f** (0.6 g, 53%). **11f**: Colorless thick oil; IR (neat) 3247, 3091, 2928, 2854, 1738, 1729, 1456, 1400, 1158, 1120, 1038, 980 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 5.71 (1H, br s, COOH), 2.59–2.19 (5H, m), 2.17–1.45 (7H, m), 1.40–1.20 (3H, m). **12f**: Thick yellow oil; IR (neat) 3091, 2929, 2857, 2103, 1734, 1698, 1641, 1451, 1376, 1148 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 5.30 (1H, br s, CHN_2), 2.60–2.20 (5H, m), 2.15–1.58 (7H, m), 1.44–1.19 (3H, m); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 215.3 (C=O), 194.8 (C=O), 54.5 (CHN_2), 50.7 (CH), 42.8 (CH_2), 38.4 (CH_2), 31.9 (CH_2), 29.3 (CH_2), 28.5 (CH_2), 27.2 (CH_2), 24.2 (CH_2). Found: C, 63.49; H, 7.76; N, 13.41%. Calcd for $C_{11}H_{16}N_2O_2$: C, 63.44; H, 7.74; N, 13.45%.

2-(4-Diazo-3-oxobutyl)-3,4-dihydronaphthalen-1(2*H*)-one (22). The hydrolysis of the ester **21** (2 g, 8.1 mmol) with an 8% aqueous potassium hydroxide solution for 5 h afforded the 3-(1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)propionic acid (1.7 g in 96%). A solution containing 1.5 g (6.9 mmol) of crude acid in dry ether was treated with 0.8 cm^3 (8.3 mmol) of ethyl chloroformate and 1.5 cm^3 (10.3 mmol) of triethylamine to afford a mixed anhydride, and a treatment with 15.8 mmol of a diazomethane solution gave the diazo ketone **22** (1 g, 60%). 3-(1-Oxo-1,2,3,4-tetrahydronaphthalen-2-yl)propionic acid: Pale orange thick oil; IR (neat) 3478, 2934, 1716, 1684, 1602, 1454, 1288, 1226, 745 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.93–7.89 (1H, m, arom-H), 7.60–7.51 (1H, m, arom-H), 7.49–7.24 (2H, m, arom-H), 4.75 (1H, br s, COOH), 3.09–2.94 (2H, m), 2.58–2.33 (3H, m), 2.27–2.08 (2H, m), 1.97–1.65 (2H, m). **22**: Dark yellow thick oil; IR (neat) 3022, 2935, 2843, 2104, 1765, 1693, 1603, 1488, 1217, 1138, 1084, 987, 754 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 8.02–7.97 (1H, m, arom-H), 7.49–7.42 (1H, m, arom-H), 7.32–7.21 (2H, m, arom-H), 5.34 (1H, br s, CHN_2), 3.04–2.98 (2H, m), 2.55–2.48 (3H, m), 2.28–2.13 (2H, m), 2.08–1.81 (2H, m); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 200.3 (C=O), 195.2 (C=O), 144.3 (arom quat-C), 133.7 (=CH), 132.8 (arom quat-C), 129.2 (=CH), 127.7 (=CH), 126.9 (=CH), 54.9 (CHN_2), 47.1 (CH), 38.7 (CH_2), 29.4 (CH_2), 28.9 (CH_2), 25.7 (CH_2). Found: C, 69.47; H, 5.89, N, 11.50%. Calcd for $C_{14}H_{14}N_2O_2$: C, 69.41; H, 5.83, N, 11.56%.

General Procedure for the Rhodium(II)-Catalyzed Cycloaddition of Diazo Ketones (12, 22) with Dipolarophiles. An oven-dried flask containing 2 equivalents of dipolarophile and appropriate diazo ketone in (8 cm^3) dry dichloromethane (dried over diphosphorus pentaoxide) was degasified under an argon atmosphere. To this reaction mixture was added (0.5 mol%) rhodium(II) acetate dimer, which was allowed to stir for 3 h under an argon atmosphere at room temperature, followed by TLC until disappearance of the starting material. The solvent was removed under reduced pressure and the residue was purified by a neutral alumina column to furnish the respective cycloadducts.

Reaction of α-Diazo Ketone 12a with *N*-Phenylmaleimide. A mixture of *N*-phenylmaleimide (285 mg, 1.6 mmol) and diazo ketone **12a** (160 mg, 0.8 mmol) in dry dichloromethane (8 cm^3) was allowed to react with (1.8 mg) rhodium(II) acetate dimer at room temperature under an argon atmosphere for 2.5 h according to the general method to afford **14a** in (165 mg, 61%). Colorless solid (from chloroform/hexane); mp 205–207 °C; IR (KBr) 2968, 2938, 1780, 1717, 1598, 1498, 1458, 1385, 1191, 1089 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.52–7.39 (3H, m, arom-H), 7.29–7.25 (2H, m, arom-H), 4.81 (1H, s, OCH), 3.69 (1H, d, J = 8.2 Hz), 3.45–3.36 (1H, m), 3.21 (1H, d, J = 8.2 Hz), 2.41–1.58 (9H, m), 1.07 (3H, d, J = 6.8 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 214.6 (C=O), 175.6 (NC=O), 175.1 (NC=O), 132.2 (quat-C), 129.3 (=CH), 128.9 (=CH), 126.4 (=CH), 95.8 (quat-C), 84.7 (OCH), 52.6 (CH), 49.1 (CH), 48.6 (CH), 38.0 (CH), 35.1 (CH_2), 31.5 (CH_2), 27.6 (CH_2), 20.6 (CH_2), 15.7 (CH_3); MS *m/z* (rel intensity) 339 (M^+; 100), 321 (10), 311 (46), 283 (21), 269 (16), 241 (47), 175 (61), 174 (40), 137 (69), 136 (18), 135 (19), 94 (80). Found: C, 70.71; H, 6.23; N, 4.12%. Calcd for $C_{20}H_{21}NO_4$: C, 70.78; H, 6.24; N, 4.13%.

Reaction of α-Diazo Ketone 12b with *N*-Phenylmaleimide. A mixture of *N*-phenylmaleimide (240 mg, 1.4 mmol) and diazo ketone **12b** (135 mg, 0.7 mmol) in dry dichloromethane (8 cm^3) was allowed to react with (1.5 mg) rhodium(II) acetate dimer at room temperature under an argon atmosphere for 3 h according to the general method to afford **14b** (138 mg, 58%). Colorless solid (from ethyl acetate/hexane); mp 185–187 °C; IR (KBr) 2961, 2873, 1777, 1715, 1494, 1459, 1390, 1196, 1090, 973, 738 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.48–7.39 (3H, m, arom-H), 7.30–7.25 (2H, m, arom-H), 4.90 (1H, s, OCH), 3.53 (1H, d, J = 8.4 Hz), 33.21 (1H, d, J = 8.4 Hz), 2.80–2.00 (4H, m), 1.90–1.17 (6H, m), 1.13 (3H, d, J = 6.8 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 213.8 (C=O), 175.5 (NCO), 175.4 (NCO), 132.2 (quat-C), 129.7 (=CH), 129.3 (=CH), 126.7 (=CH), 97.6 (quat-C), 85.3 (OCH), 53.5 (CH), 48.8 (CH), 48.1 (CH), 42.4 (CH_2), 38.4 (CH_2), 28.2 (CH_2), 25.9 (CH_2), 23.3 (CH_2), 19.1 (CH_3); MS *m/z* (rel intensity) 339 (M^+; 86), 321 (26), 282 (55), 267 (34), 188 (16), 175 (100), 174 (56), 166 (48), 136 (30), 135 (41). Found: C, 70.69; H, 6.21; N, 4.09%. Calcd for $C_{20}H_{21}NO_4$: C, 70.78; H, 6.24; N, 4.13%.

Reaction of α-Diazo Ketone 12c with *N*-Phenylmaleimide. A mixture of *N*-phenylmaleimide (240 mg, 1.4 mmol) and diazo ketone **12c** (135 mg, 0.7 mmol) in dry dichloromethane (8 cm^3) was allowed to react with (1.5 mg) rhodium(II) acetate dimer at room temperature under an argon atmosphere for 3 h according to the general method to afford **14c** (116 mg, 49%). Colorless solid (from ethyl acetate/hexane); mp 177–179 °C; IR (KBr) 2956, 2876, 1718, 1496, 1456, 1387, 1198 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.47–7.39 (3H, m, arom-H), 7.29–7.25 (2H, m, arom-H), 4.83 (1H, s, OCH), 3.55 (1H, d, J = 8.4 Hz), 3.29 (1H, d, J = 8.4 Hz), 2.95–1.99 (5H, m), 1.95–1.17 (5H, m), 1.19 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 212.4 (C=O), 175.8 (NCO), 173.7 (NCO), 132.2 (quat-C), 129.6 (=CH), 129.2 (=CH), 126.6 (=CH), 97.5 (quat-C), 86.3 (OCH), 52.0 (CH), 51.1 (quat-C), 48.1 (CH), 42.3 (CH_2), 32.0 (CH_2), 27.4 (CH_2), 26.1 (CH_2), 17.4 (CH_2), 14.9 (CH_3); MS *m/z* (rel intensity) 339 (M^+; 61), 321 (24), 311 (17),

283 (20), 282 (19), 255 (12), 175 (65), 174 (35), 167 (21), 138 (20), 137 (34), 136 (27), 135 (24). Found: C, 70.81; H, 6.29; N, 4.06%. Calcd for $C_{20}H_{21}NO_4$: C, 70.78; H, 6.24; N, 4.13%.

Reaction of α-Diazo Ketone 12d with *N*-Phenylmaleimide. A mixture of *N*-phenylmaleimide (350 mg, 2 mmol) and diazo ketone **12d** (200 mg, 1 mmol) in dry dichloromethane (10 cm^3) was allowed to react with (2.2 mg) rhodium(II) acetate dimer at room temperature under an argon atmosphere for 2 h according to the general method to afford **14d** (193 mg, 57%). Colorless solid (from chloroform/hexane) mp 206–208 °C; IR (KBr) 2933, 2864, 1777, 1712, 1493, 1458, 1393, 1202, 1090 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.47–7.39 (3H, m, arom-H), 7.29–7.24 (2H, m, arom-H), 4.85 (1H, s, OCH), 3.57 (1H, d, J = 8.4 Hz), 3.35 (1H, d, J = 8.4 Hz), 3.20–3.05 (1H, m), 2.35–2.23 (1H, m), 2.02–1.26 (11H, m); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 214.2 (C=O), 175.3 (NC=O), 174.9 (NC=O), 131.6 (quat-C), 129.3 (=CH), 128.9 (=CH), 126.3 (=CH), 90.0 (quat-C), 85.1 (OCH), 53.0 (CH), 52.7 (CH), 45.0 (CH), 37.4 (CH_2), 36.2 (CH_2), 28.0 (CH_2), 25.7 (CH_2), 25.4 (CH_2), 22.6 (CH_2); MS *m/z* (rel intensity) 339 (M^+; 69), 321 (35), 312 (17), 282 (12), 175 (100), 174 (48), 166 (15), 148 (17), 138 (32), 137 (88). Found: C, 70.84, H, 6.26; N, 4.19%. Calcd for $C_{20}H_{21}NO_4$: C, 70.78; H, 6.24; N, 4.13%.

Reaction of α-Diazo Ketone 12e with *N*-Phenylmaleimide. A mixture of *N*-phenylmaleimide (140 mg, 0.8 mmol) and diazo ketone **12e** (75 mg, 0.4 mmol) in dry dichloromethane (5 cm^3) was allowed to react with (0.7 mg) rhodium(II) acetate dimer at room temperature under an argon atmosphere for 2.5 h according to the general method to afford **14e** (81 mg, 58%). Colorless solid (from chloroform/hexane) mp 211–213 °C; IR (KBr) 2863, 1776, 1711, 1455, 1392, 1089 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.52–7.39 (3H, m, arom-H), 7.29–7.25 (2H, m, arom-H), 4.81 (1H, s, OCH), 3.40 (1H, d, J = 8.4 Hz), 3.10 (1H, d, J = 8.4 Hz), 3.22–3.04 (1H, m), 2.35–2.22 (1H, m), 2.12–1.26 (10H, m), 1.08 (3H, d, J = 6.8 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 214.3 (C=O), 175.4 (NC=O), 174.8 (NC=O), 131.5 (quat-C), 129.3 (=CH), 128.9 (=CH), 126.3 (=CH), 90.1 (quat-C), 85.2 (OCH), 53.1 (CH), 52.6 (CH), 45.0 (CH), 37.8 (CH), 35.9 (CH_2), 28.1 (CH_2), 25.6 (CH_2), 25.4 (CH_2), 22.7 (CH_2), 14.9 (CH_3); MS *m/z* 353 (M^+). Found: C, 71.41, H, 6.58; N, 3.93%. Calcd for $C_{21}H_{23}NO_4$: C, 71.37; H, 6.56; N, 3.96%.

Reaction of α-Diazo Ketone 12f with *N*-Phenylmaleimide. A mixture of *N*-phenylmaleimide (350 mg, 2 mmol) and diazo ketone **12f** (210 mg, 1 mmol) in dry dichloromethane (10 cm^3) was allowed to react with (2.2 mg) rhodium(II) acetate dimer at room temperature under an argon atmosphere for 3 h according to the general method to afford **14f** (226 mg, 64%). Colorless solid (from chloroform/hexane) mp 217–219 °C; IR (KBr) 2928, 2859, 1777, 1709, 1493, 1396, 1195, 1094, 1027 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.52–7.36 (3H, m, arom-H), 7.30–7.26 (2H, m, arom-H), 4.81 (1H, s, OCH), 3.62 (1H, d, J = 8.4 Hz), 3.36 (1H, d, J = 8.4 Hz), 3.16–3.03 (1H, m), 2.36–1.26 (14H, m); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 214.2 (C=O), 175.3 (NC=O), 174.9 (NC=O), 131.7 (quat-C), 129.3 (=CH), 128.9 (=CH), 126.3 (=CH), 94.2 (quat-C), 84.1 (OCH), 54.2 (CH), 53.6 (CH), 49.9 (CH), 38.6 (CH_2), 37.4 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 28.5 (CH_2), 27.9 (CH_2), 21.9 (CH_2); MS *m/z* (rel intensity) 353 (M^+; 40), 335 (13), 325 (14), 175 (56), 174 (56), 152 (31), 151 (71), 150 (35), 135 (23), 132 (10), 91 (72), 55 (100). Found: C, 71.41, H, 6.58; N, 3.96%. Calcd for $C_{21}H_{23}NO_4$: C, 71.37; H, 6.56; N, 3.96%.

Reaction of α-Diazo Ketone 12a with DMAD. A mixture of DMAD (75 mg, 0.5 mmol) and diazo ketone **12a** (50 mg, 0.25 mmol) in dry dichloromethane (5 cm^3) was allowed to react with (0.6 mg) rhodium(II) acetate dimer at room temperature under an argon atmosphere for 1.5 h according to the general method to afford 7-methyl-8-oxo-12-oxatricyclo[7.2.1.$0^{1,5}$]dodec-10-ene-10,11-dicarboxylic acid dimethyl ester (**15g**, 42 mg, 54%). Colorless thick oil; IR (neat) 2960, 2941, 1731, 1719, 1590, 1502, 1450, 1360, 1201, 1090, 980 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 5.10 (1H, s, OCH), 3.86 (3H, s, OCH_3), 3.78 (3H, s, OCH_3), 3.41–3.30 (1H, m), 2.38–1.59 (9H, m), 1.10 (3H, d, J = 6.8 Hz, CH_3); MS *m/z* 308 (M^+). Found: C, 62.27; H, 6.57%. Calcd for $C_{16}H_{20}O_6$: C, 62.33; H, 6.54%.

Reaction of α-Diazo Ketone 12b with DMAD. A mixture of DMAD (150 mg, 1 mmol) and diazo ketone **12b** (100 mg, 0.5 mmol) in dry dichloromethane (5 cm^3) was allowed to react with (1.1 mg) of rhodium(II) acetate dimer at room temperature under an argon atmosphere for 2.5 h according to the general method to afford 2-methyl-8-oxo-12-oxatricyclo[7.2.1.$0^{1,5}$]dodec-10-ene-10,11-dicarboxylic acid dimethyl ester (**15h**, 94 mg, 61%). Colorless thick oil; IR (neat) 2957, 1726, 1650, 1281, 909 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 5.13 (1H, s, OCH), 3.82 (3H, s, OCH_3), 3.80 (3H, s, OCH_3), 3.20–2.25 (5H, m), 2.05–1.04 (5H, m), 1.02 (3H, d, J = 6.8 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 210.6 (C=O), 165.1 (COO), 161.9 (COO), 144.8 (quat-C), 134.7 (quat-C), 104.1 (quat-C), 88.2 (OCH), 53.0 (OCH_3), 52.9 (OCH_3), 49.5 (CH), 45.5 (CH), 39.0 (CH_2), 32.6 (CH_2), 29.7 (CH_2), 24.8 (CH_2), 16.4 (CH_3); MS *m/z* 308 (M^+). Found: C, 62.21, H, 6.47%. Calcd for $C_{16}H_{20}O_6$: C, 62.33; H, 6.54%.

Reaction of α-Diazo Ketone 12c with DMAD. A mixture of DMAD (150 mg, 1 mmol) and diazo ketone **12c** (100 mg, 0.5 mmol) in dry dichloromethane (5 cm^3) was allowed to react with (1.1 mg) rhodium(II) acetate dimer at room temperature under an argon atmosphere for 3 h according to the general method to afford 5-methyl-8-oxo-12-oxatricyclo[7.2.1.$0^{1,5}$]dodec-10-ene-10,11-dicarboxylic acid dimethyl ester (**15i**, 71 mg, 45%). Colorless thick oil; IR (neat) 3024, 2956, 2882, 1728, 1656, 1438, 1326, 1271, 1233, 1055, 757 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 5.02 (1H, s, OCH), 3.88 (3H, s, OCH_3), 3.77 (3H, s, OCH_3), 3.00–2.50 (3H, m), 2.45–1.25 (7H, m), 1.21 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 207.4 (C=O), 164.2 (COO), 161.5 (COO), 151.1 (quat-C), 130.4 (quat-C), 103.5 (quat-C), 88.4 (OCH), 53.3 (OCH_3), 52.9 (OCH_3), 51.1 (quat-C), 41.0 (CH_2), 34.5 (CH_2), 32.3 (CH_2), 31.0 (CH_2), 21.4 (CH_2), 18.8 (CH_3); MS *m/z* (rel intensity) 308 (M^+; 5), 276 (30), 249 (27), 248 (32), 234 (21), 220 (18), 210 (27), 202 (31), 198 (27), 189 (58), 179 (55), 178 (32), 153 (25), 133 (21), 55 (100). Found: C, 62.39; H, 6.49%. Calcd for $C_{16}H_{20}O_6$: C, 62.33; H, 6.54%.

Reaction of α-Diazo Ketone 12d with Rhodium(II) Acetate Dimer. A solution of diazo ketone **12d** (100 mg, 0.5 mmol) in dry dichloromethane (5 cm^3) was allowed to react with (1.1 mg) rhodium(II) acetate dimer at room temperature under an argon atmosphere for 3.5 h according to the general method to afford 4,5,6,7,8,9-hexahydrobenzo[*b*]oxepin-3-one (**16d**, 58 mg, 69%). Colorless thick oil; IR (neat) 2930, 1716, 1449, 1371, 1140, 1025 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 4.26 (2H, s, OCH_2), 2.92–2.85 (2H, m), 2.18–1.23 (10H, m); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 213.4 (C=O), 152.5 (quat-C), 114.1 (quat-C), 78.4 (OCH_2), 40.1 (CH_2), 30.5 (CH_2), 29.4 (CH_2), 29.2 (CH_2), 23.4 (CH_2), 22.9 (CH_2); MS *m/z* (rel intensity) 166 (M^+; 45), 165 (20), 164 (17), 153 (44), 152 (19), 151 (27), 145 (13), 141 (20), 139 (25), 55 (100). Found: C, 72.21; H, 8.45%. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49%.

Reaction of α-Diazo Ketone 12d with *p*-Benzoquinone (17): A mixture of *p*-benzoquinone (215 mg, 2 mmol) and diazo ketone **12d** (195 mg, 1 mmol) was allowed to react with rhodium(II) acetate dimer (2.2 mg) in dichloromethane solution (10 cm^3) at room temperature under an argon atmosphere for 2.5 h according to the general method to afford three products **18**, **19**, and **20** in 40% overall yield. **18**: (49 mg, 18%), mixture of diastereomers in the ratio of 1:0.7, colorless solid (from chloroform/hexane) mp 156–158 °C; IR (KBr) 2935, 2861, 1715, 1675, 1635, 1449, 1228, 1207, 1149, 1089, 1053 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.25–7.15 (1H, m), 6.99–6.91 (1H, m), 6.52–6.16 (2H, m), 4.33 (1H, s, OCH), 3.10–2.89 (1H, m), 2.47–1.22 (12H, m); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 211.7 (C=O), 184.6 (C=O), 147.1 (=CH), 142.5 (=CH), 131.3 (=CH), 127.5 (=CH), 116.1 (quat-C), 86.6 (OCH), 78.6 (quat-C), 47.0 (CH), 41.6 (CH_2), 38.8 (CH_2), 30.9 (CH_2), 25.1 (CH_2), 24.9 (CH_2), 23.8 (CH_2); MS *m*/*z* 274 (M^+). Found: C, 69.88; H, 6.70%. Calcd for $C_{16}H_{18}O_4$: C, 70.06; H, 6.61%. **19**: (16 mg, 6%), thick oil; IR (neat) 2932, 2911, 1732, 1675, 1610, 1460, 1271, 1252, 1036, 913 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.91 (1H, d, J = 10.4 Hz), 6.84 (1H, d, J = 10.4 Hz), 4.69 (1H, s, OCH), 3.27 (1H, d, J = 8.4 Hz), 3.20 (1H, d, J = 8.4 Hz), 2.80–1.24 (13 H, m); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 202.6 (C=O), 193.0 (C=O), 192.9 (C=O), 143.1 (=CH), 142.6 (=CH), 92.8 (quat-C), 86.2 (OCH), 52.3 (CH), 51.4 (CH), 43.5 (CH), 41.6 (CH_2), 38.7 (CH_2), 30.8 (CH_2), 25.1 (CH_2), 24.9 (CH_2), 23.9 (CH_2); MS *m*/*z* 274 (M^+). Found: C, 70.19; H, 6.54%. Calcd for $C_{16}H_{18}O_4$: C, 70.06; H, 6.61%. **20**: (44 mg, 16%), colorless solid (from ethyl acetate/hexane) mp 172–174 °C; IR (KBr) 3433, 3075, 2934, 1170, 1663, 1173, 823 cm^{-1}; ^{1}H NMR ($CDCl_3$/DMSO-d_6, 200 MHz) δ 6.95 (1H, d, J = 10.2 Hz), 6.08 (1 H, d, J = 10.2 Hz), 4.78 (1 H, s, OCH), 2.95–2.85 (2H, m), 2.60 (1H, s, OH), 1.90–1.12 (14H, m); ^{13}C NMR ($CDCl_3$/DMSO-d_6, 50.3 MHz) δ 196.9 (C=O), 148.2 (=CH), 129.6 (=CH), 115.3 (quat-C), 110.9 (quat-C), 91.0 (OCH), 89.5 (quat-C), 80.3 (OCH), 46.2 (CH_2), 43.7 (CH), 38.9 (CH_2), 36.8 (CH_2), 31.4 (CH_2), 26.5 (CH_2), 24.9 (CH_2), 24.2 (CH_2); MS *m*/*z* (rel intensity) 292 (M^+; 15), 261 (31), 247 (39), 246 (36), 186 (29), 153 (91), 152 (39), 151 (27), 54 (100). Found: C, 64.74; H, 6.52%. Calcd for $C_{16}H_{20}O_5$: C, 65.74; H, 6.89%.

Reaction of α-Diazo Ketone 22 with *N*-Phenylmaleimide. A mixture of *N*-phenylmaleimide (350 mg, 2 mmol) and diazo ketone **22** (250 mg, 1 mmol) in dry dichloromethane (10 cm^3) was allowed to react with (2.2 mg) rhodium(II) acetate dimer at room temperature under an argon atmosphere for 3.5 h according to the general method to afford **24** (155 mg, 40%) and rearranged product **25** (28 mg, 13%). **24**: Colorless solid (from chloroform/hexane) mp 179–181 °C; IR (KBr) 3023, 2932, 2865, 1782, 1716, 1598, 1497, 1453, 1382, 1191, 1085 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.48–7.15 (9H, m, arom-H), 4.98 (1H, s, OCH), 4.04 (1H, d, J = 8.4 Hz), 3.47 (1H, d, J = 8.4 Hz), 3.17–3.08 (1H, m), 2.83–2.76 (2H, m), 2.62–2.48 (1H, m), 2.16–2.04 (2H, m), 1.78–1.65 (3H, m); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 214.0 (C=O), 176.2 (NC=O), 173.5 (NC=O), 138.5 (quat-C), 133.0 (quat-C), 132.1 (quat-C), 129.6 (=CH), 129.1 (=CH), 128.9 (=CH), 128.8 (=CH), 127.9 (=CH), 126.5 (=CH), 126.4 (=CH), 90.2 (quat-C), 85.7 (OCH), 57.4 (CH), 51.7 (CH), 45.3 (CH), 40.1 (CH_2), 27.8 (CH_2), 26.8 (CH_2), 25.2 (CH_2); MS *m*/*z* (rel intensity) 387 (M^+; 100), 369 (21), 222 (17), 186 (39), 185 (17), 184 (29), 183 (18), 178 (14), 167 (15), 165 (20), 156 (15), 155 (17), 153 (17), 141(30). Found: C, 74.41; H, 5.49; N, 3.66%. Calcd for $C_{24}H_{21}NO_4$: C, 74.40; H, 5.46; N, 3.62%.

4,5,6,7-Tetrahydronaphtho[1,2-*b*][1]oxepin-3(2*H*)-one (25): Colorless thick oil; IR (neat) 3066, 2929, 2835, 1725, 1680, 1657, 1602, 1486, 1432, 1374, 1324, 1135, 1094 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.46–7.42 (1H, m, arom-H), 7.24–7.12 (3H, m, arom-H), 4.45 (2H, s, OCH_2), 3.09–3.02 (2H, m), 2.82–2.74 (2H, m), 2.52–2.45 (2H, m), 2.29–2.22 (2H, m); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 212.5 (C=O), 149.6 (quat-C), 135.4 (quat-C), 132.3 (quat-C), 127.4 (=CH), 127.0 (=CH), 126.5 (=CH), 121.1 (=CH), 118.5 (quat-C), 78.9 (OCH_2), 39.4 (CH_2), 29.5(CH_2), 28.8 (CH_2), 27.7 (CH_2); MS *m*/*z* 214 (M^+). Found: C, 78.41; H, 6.57%. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59%.

X-ray Crystal Structure Analysis of Compound 24. Crystal data for the 1-tetralone derived cyclooctane derivative **24**: $C_{24}H_{21}NO_4$, M_r = 387.42, 0.10×0.06×0.04 mm, Monoclinic, $P2_1/a$, a = 11.275(5) Å, b = 12.927(3) Å, c = 13.791(5) Å, β = 113.30(3)°, V = 1846.1(11) $Å^3$, T = 293(2) K, R_1 = 0.0912, wR_2 = 0.2240 on observed data, Z = 4, $D_{calc.}$ = 1.394 Mg m^{-3}, $F(000)$ = 816, Absorption coefficient = 0.095 mm^{-1}, λ = 7107 Å, 2402 reflections were collected on a CAD-4 diffractometer, 989 observed reflections ($I \geq 2\sigma(I)$). The largest difference peak and hole = 0.353 and −0.305e $Å^{-3}$, respectively. The structure was solved by direct methods and refined by full-matrix least squares on F^2 using SHELX-97.[33] Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and deposition numbers CCDC 174919. The data are also deposited as Document No. 75014 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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