8.21 (d, 4 H, *o*-Ar), 7.85 (t, 4 H, *p*-Ar), 7.79 (d, 4 H, *m*-Ar), 7.66 (t, 4 H, *m'*-Ar), 5.38 (s, 4 H, NHCO), 0.10 (s, 36 H, CH_3), −2.44 (s, 2 H, NH pyr).

5,10,15,20-Tetrakis(*o*-pivalamidophenyl)porphyrin (TpivPP). This compound was synthesized following the procedure described by Collman et al.[4]

Zinc and Copper Complexes of Porphyrins. Insertion of zinc and copper into the free-base porphyrins was accomplished using $ZnCl_2$ and $CuCl_2$ in tetrahydrofuran, in the presence of 2,6-dimethylpyridine at 50–60 °C for 1 h. The crude metalloporphyrins were purified by TLC over silica gel plates with methylene chloride/acetone (5/1 v/v) as eluant and crystallized by low evaporation of CH_2Cl_2/hexane (1/2 v/v, 70%). Zn–1: λ_{max}/nm (ϵ/mmol L^{-1}) 425 (370.5), 555 (15.8), 605 (3.7); ^1H NMR (CD_2Cl_2) δ 8.68 (s, 8 H, H_{pyr}, 8.06 (d, 4 H, *o*-Ar), 7.78 (t, 4 H, *p*-Ar), 7.64 (d, 4 H, *m*-Ar), 7.56 (t, 4 H, *m'*-Ar), 6.20 (s, 4 H, NHCO), 0.33 (s, 36 H, CH_3).

Cu–1: λ_{max}/nm (ϵ/mmol L^{-1}) 419 (128.8), 542.5 (4.8), 577.5 (0.8).

Acknowledgment. This work was supported by the Institut National de la Santé et de la Recherche Medicale. A grant from the State Scholarships Foundation, Republic of Greece, to L.L. is gratefully acknowledged. We thank Dr. J. L. Guerquin for recording the ^1H NMR spectra.

Registry No. 1, 123811-58-5; Zn-1, 123811-59-6; Cu-1, 123811-60-9; **2** (α,α,α,α isomer), 123878-56-8; **2** (α,α,α,β isomer), 123878-57-9; **2** (α,α,β,β isomer), 123878-58-0; **2** (α,β,α,β isomer), 123878-59-1; **3** (α,α,α,α isomer), 123878-60-4; **3** (α,α,α,β isomer), 123878-61-5; **3** (α,α,β,β isomer), 123878-62-6; **3** (α,β,α,β isomer), 123878-63-7; **4** (α,α,α,α isomer), 123811-56-3; **4** (α,α,α,β isomer), 123878-64-8; **4** (α,α,β,β isomer), 123878-65-9; **4** (α,β,α,β isomer), 123878-66-0; **5** (α,α,α,α isomer), 123811-57-4; **5** (α,α,α,β isomer), 123878-67-1; **5** (α,α,β,β isomer), 123878-68-2; **5** (α,β,α,β isomer), 123878-69-3; Zn–(TpivPP), 86782-69-6; Cu–(TpivPP), 86727-67-5; *o*-cyanobenzaldehyde, 7468-67-9; pyrrole, 109-97-7.

Site Selectivity of Diels–Alder Reactions of a Bicyclic, Heteroannular Dienone[1]

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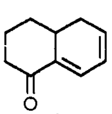
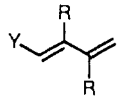
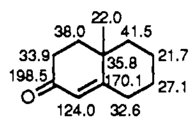
In a recent study of Diels–Alder reactions of cycloalkenones it was shown that the interaction of 3,4,4a,5-tetrahydronaphthalen-(2*H*)-1-one (**1**) with (*E*)-1-methoxy-1,3-butadiene (**2a**) under Yb(fod)$_3$ catalysis led exclusively to cycloaddition at the dienophile's α,β double-bond site and the formation of a spiro tricycle.[3] The absence of any adduct of the hydroanthracene type illustrated the sharp difference of reactivity of the two olefinic sites in the dienone.[3] This interesting result pointed to the need of exploration of Diels–Alder reactions of structurally varying dienones.



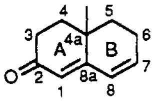
1



2a, R = H, Y = OMe
b, R = Me, Y = H



3



4

Table I. Reaction Conditions of the Diels–Alder Reactions of Dienes 2 with Dienone 4[a]

diene	diene/ ketone[b]	temp, °C	time, h	products	product yield,[c] %
2a	4.5	170	69	2.7:1 **5a** and **5b**[g]	56
2b	12	170	96	**6**[g]	17
2a[d,e]	6	100	120	5.2:1 **5a** and **5b**	27
2b[d,f]	4.5	75	47	**6**	35

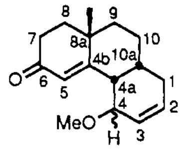
[a] In dry toluene. [b] Ratio of equivalents. [c] GC based. [d] Complexation time, 40 min;[4b] complexation temperature, 22 °C.[4b] [e] Yb(fod)$_3$/ketone equivalents ratio, 0.25; concentration, 0.2 M. [f] $AlCl_3$/ketone equivalents ratio, 0.5; concentration, 0.2 M. [g] Plus two products of unknown constitution accounting for 14 and 12% of the total product mixture from **2a** and **2b**, respectively.

The present note reports on the cycloadditions of 4a-methyl-4,4a,5,6-tetrahydronaphthalen-2(3*H*)-one (**4**) with (*E*)-1-methoxy-1,3-butadiene (**2a**) and with 2,3-dimethyl-1,3-butadiene (**2b**). In view of dienone **4** containing a structure component of the 3-alkyl-2-cyclohexenone type—a system known not to undergo Diels–Alder reaction[4]—the the dienophile could be expected to behave differently from dienone **1** and perhaps show preference for addition across its γ,δ olefinic linkage. The reactive, electron-rich dienes **2** were chosen for the present study to compensate for the expected low reactivity of the reaction partner **4**.

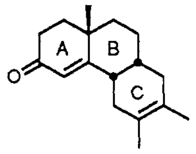
Diels–Alder Reaction Products

The cycloadditions of dienone **4**, prepared from 10-methyl-$\Delta^{1(9)}$-octal-2-one[5] (**3**) by dehydrogenation with chloranil,[6] were performed with various diene–dienophile combinations under thermal as well as acid-catalyzed (aluminum trichloride and ytterbium tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedioate)[7]) conditions, leading to adducts in 17–56% yields (Table I).

The product structures revealed the cycloaddition to have taken place exclusively on the side of dienone **4** opposite to its angular methyl group, methoxybutadiene **2a** leading to the formation of adducts **5a** and **5b** and dimethylbutadiene **2b** furnishing tricycle **6**. The methoxybutadiene reaction favored endo addition (the **5a**/**5b** ratio being ca. 3), which tendency was enhanced on Yb(fod)$_3$ catalysis (**5a**/**5b** ratio of ca. 5).



5a, 4β-H
b, 4α-H



6

The structures of the three products were determined in the following manner. The infrared carbonyl absorption band (ca. 1657 cm^{-1}) and the ^{13}C NMR signal of the carbonyl group (ca. 199 ppm), characteristic of a conjugated enone unit, show the cycloaddition to have occurred in ring B of dienone **4**. Furthermore, the strong similarity of the chemical shifts of the angular methyl group and the ring

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[1] (a) Publication 17 of the series "Diels–Alder Reactions of Cycloalkenones. (b) For the previous paper see: Fringuelli, F.; Guo, M.; Minuti, L.; Pizzo, F.; Taticchi, A.; Wenkert, E. *J. Org. Chem.* **1989**, *54*, 710.

[2] (a) University of California. (b) Università di Perugia.

[3] Fringuelli, F.; Minuti, L.; Radics, L.; Taticchi, A.; Wenkert, E. *J. Org. Chem.* **1988**, *53*, 4607.

[4] (a) Nagakura, I.; Ogata, H.; Ueno, M.; Kitahara, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2995. (b) Fringuelli, F.; Pizzo, F.; Taticchi, A.; Wenkert, E. *J. Org. Chem.* **1983**, *48*, 2802.

[5] Heathcock, C. H.; Ellis, J. E.; McMurry, J. E.; Coppolino, A. *Tetrahedron Lett.* 1971, 4995.

[6] Agnello, E. J.; Laubach, G. D. *J. Am. Chem. Soc.* **1960**, *82*, 4293.

[7] (a) Bednarski, M.; Danishefsky, S. *J. Am. Chem. Soc.* **1983**, *105*, 3716. (b) Danishefsky, S.; Bednarski, M. *Tetrahedron Lett.* **1984**, 721.

0022-3263/89/1954-6138$01.50/0

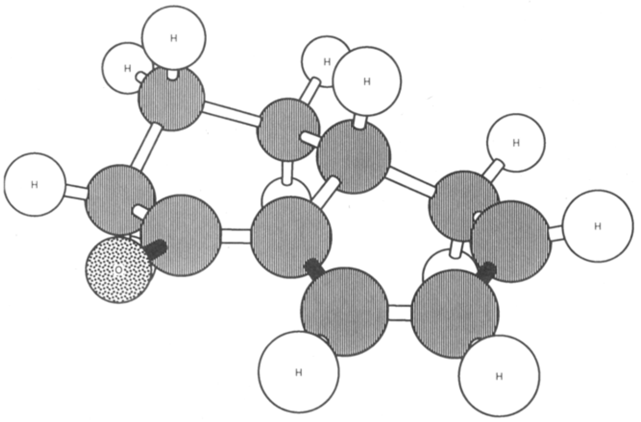

Figure 1. Compound 1.

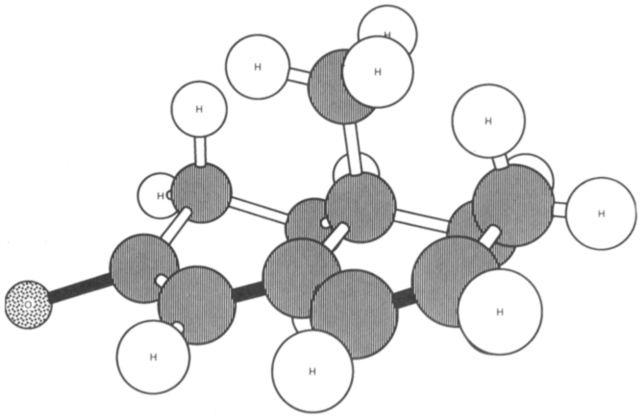

Figure 2. Compound 4.

A carbons (except for C(4b)) of the adducts with like carbons of model **3** (δ values being shown on the formula)[8] confirm this conclusion. The over 4 ppm shielding of C(9) of the adducts (vs this shift in model **3**) indicate the axiality of C(1) toward ring B and hence the α-cis B–C ring fusion. The consequent H(4a)–H(10a) cis configuration is in consonance with the low coupling characteristics (ca. 4 Hz) of H(4a). COSY experiments on all three adducts, revealing minimal coupling between H(5) and H(4a), established the latter's allylic site and δ value. The *J* values of H(4a) in compounds **5** vs **6** uncovered both the regiochemistry and stereochemistry of the methoxy group of ethers **5**. Two further facts are in consonance with the stereochemistry assignment of the ethers: (a) the low-field position of the H(5) signal in the ^{1}H NMR spectrum of substance **5a** (vs **5b** and **6**) exhibiting the anisotropy of the proximate methoxy group and (b) the ca. 5 ppm shielding of C(10a) (i.e., a γ-effect) of ether **5b** (vs **5a** and **6**) revealing the 1,3-diaxial H(10a)–OMe interaction.

The above results illustrate the difference of regiochemistry behavior of dienones **1** and **4** in cycloaddition processes, the latter preferring Diels–Alder reactions across its γ,δ double bond (see Figures 1 and 2). The antidiastereofacial selectivity of the above additions agrees with theory,[9] i.e., the necessity of axial approach of the diene at C(7) antiparallel to pseudo-axial H(6). The ready formation of tricycles **5** and **6** constitutes a new hydrophenanthrone synthesis, whose exploitation is the subject of further investigation.

Experimental Section

The melting points were taken on a Büchi melting point apparatus and are uncorrected. Infrared spectra of chloroform solutions were recorded on a Perkin-Elmer 257 spectrophotometer. ^{1}H and ^{13}C NMR spectra of $CDCl_3$ solutions were obtained on a Nicolet QE-300 spectrometer, operating in the Fourier transform mode at 300 and 75.5 MHz, respectively. The carbon shifts (including those on formula **3**) are in parts per million downfield from Me_4Si: $\delta(Me_4Si) = \delta(CDCl_3) + 76.9$ ppm. Mass spectra were observed on a Hewlett-Packard 5970 GC-MS instrument, calibrated with perfluorotributylamine for 70-eV operation. Analytical GC was carried out with Carlo Erba HRGC (with 30 m, 0.32-mm diameter SP-2340 fused silica capillary column and with an "on column" injection system) and Hewlett-Packard 5880A (with 30 m, 0.25-mm diameter SPB-5 capillary column and with an "on column" injection system) gas chromatographs. Column chromatography was executed on 0.040–0.063 mm, 230-240 mesh ASTM Merck silica gel (50:1 reaction product/SiO_2 weight ratio). The ethers **5** were separated by gradient elution with 4:1 to 1:1 petroleum ether–ethyl acetate mixtures, and ketone **6** was eluted with 9:1 petroleum ether–ether.

4a-Methyl-4,4a,5,6-tetrahydronaphthalen-2(3*H*)-one (4). A stirring mixture of 12.0 g (73 mmol) of ketone **3**[5] and 53.5 g (220 mmol) of chloranil in 2.0 L of *tert*-butyl alcohol was refluxed under nitrogen for 3 h.[6] The mixture was filtered, and the filtrate concentrated under vacuum. A chloroform solution of the residue was washed with saturated brine, 5% potassium hydroxide solution, and water and then evaporated. Distillation of the residue yielded 7.2 g (60%) of colorless, liquid ketone **4**:[10,11] bp 77–79 °C/0.4 Torr (lit.[10] bp 80–86 °C/0.25 Torr); IR C═O 1660 (s), C═C 1620 (w) cm^{-1}; ^{1}H NMR δ 1.18 (s, 3, Me), 5.67 (br s, 1 H-1), 6.14 (dm, 1, *J* = 10 Hz, H-8), 6.22 (dm, 1, *J* = 10 Hz, H-7); ^{13}C NMR δ 21.2 (Me), 23.5 (C-6), 33.3 (C-4a), 34.2 (C-3), 35.9 (C-4), 37.1 (C-5), 123.5 (C-1), 127.8 (C-8), 137.7 (C-7), 161.7 (C-8a), 199.3 (C═O).

Diels–Alder Reactions. Both thermal and catalyzed reactions and their workup followed earlier procedures.[3,12] The reaction conditions are detailed in Table I.

8aβ-Methyl-4α-methoxy-1,4,4aβ,8,8a,9,10,10aβ-octahydro-6(7*H*)-phenanthrenone (5a): colorless, crystalline solid; mp 96–98 °C (C_6H_{14}); IR C═O 1660 (s), C═C 1612 (m) cm^{-1}; ^{1}H NMR δ 1.31 (s, 3, Me), 1.5–2.5 (m, 11, CH, methylenes), 3.08 (dd, 1, *J* = 4, 4 Hz, H-4a), 3.24 (s, 3, OMe), 4.15 (dd, 1, *J* = 4, 2 Hz, H-4), 5.52 (dm, 1, *J* = 10 Hz, H-2), 5.70 (br d, 1, *J* = 10 Hz, H-3), 6.36 (s, 1, H-5); ^{13}C NMR δ 23.6 (Me), 26.0 (C-1 or C-10), 26.5 (C-10 or C-1), 33.6 (C-7), 36.1 (C-10a), 36.5 (C-8a), 37.0 (C-9), 38.4 (C-8), 40.4 (C-4a), 50.7 (OMe), 78.7 (C-4), 126.0 (C-5), 126.5 (C-2), 127.2 (C-3), 163.5 (C-4b), 199.5 (C═O); MS, *m/e* 246 (M$^+$, 5), 91 (23), 84 (base), 69 (24).

Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 78.36; H, 8.97.

8aβ-Methyl-4β-methoxy-1,4,4aβ,8,8a,9,10,10aβ-octahydro-6(7*H*)-phenanthrenone (5b): colorless liquid; IR C═O 1655 (s), C═C 1610 (m) cm^{-1}; ^{1}H NMR δ 1.32 (s, 3, Me), 1.5–2.5 (m, 11, CH, methylenes), 2.78 (d, 1, *J* = 4 Hz, H-4a), 3.39 (s, 3, OMe), 3.73 (d, 1, *J* = 3 Hz, H-4), 5.59 (s, 1, H-5), 5.8–6.0 (m, 2, H-2, H-3); ^{13}C NMR δ 23.1 (Me), 25.7 (C-1 or C-10), 25.8 (C-10 or C-1), 31.0 (C-10a), 33.5 (C-7), 36.3 (C-8a), 37.5 (C-9), 38.2 (C-8), 41.8 (C-4a), 56.3 (OMe), 73.2 (C-4), 123.2 (C-2), 123.4 (C-5), 132.2 (C-3), 167.9 (C-4b), 198.9 (C═O); MS, *m/e* 246 (M$^+$, 8), 214 (18), 143 (14), 129 (13), 91 (19), 84 (base), 69 (13).

Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.95; H, 9.01.

2,3,8aβ-Trimethyl-1,4,4aβ,8,8a,9,10,10aβ-octahydro-6-(7*H*)-phenanthrenone (6): colorless, liquid; IR C═O 1655 (s), C═C 1605 (m) cm^{-1}; ^{1}H NMR δ 1.28 (s, 3, Me), 1.4–2.6 (m, 13, CH, methylenes), 1.53, 1.63 (s, 3 each, C-2 and C-3 methyls), 2.70 (dd, 1, *J* = 4, 4 Hz, H-4a), 5.58 (s, 1, H-5); ^{13}C NMR δ 18.4 (C-2

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[8] Cf.: Buckwalter, B. L.; Burfitt, I. R.; Nagel, A. A.; Wenkert, E.; Näf, F. *Helv. Chim. Acta* **1975**, *58*, 1567.

[9] (a) Angell, E. C.; Fringuelli, F.; Pizzo, F.; Porter, B.; Taticchi, A.; Wenkert, E. *J. Org. Chem.* **1986**, *51*, 2642. (b) Angell, E. C.; Fringuelli, F.; Pizzo, F.; Taticchi, A.; Wenkert, E. *Ibid.* **1988**, *53*, 1424.

[10] Gunstone, F. D.; Tulloch, A. P. *J. Chem. Soc.* **1955**, 1130.

[11] UV (MeOH) λ_{max} 277 nm (log ε 4.12) [lit.[10] UV (EtOH) λ_{max} 281 nm (log ε 4.22)].

[12] Fringuelli, F.; Pizzo, F.; Taticchi, A.; Halls, T. D. J.; Wenkert, E. *J. Org. Chem.* **1982**, *47*, 5056.

or C-3 Me), 18.8 (C-3 or C-2 Me), 23.1 (C-8a), 25.9 (C-10), 31.8 (C-1), 33.6 (C-4, C-7), 35.5 (C-10a), 36.1 (C-8a), 36.9 (C-9), 37.6 (C-4a), 38.4 (C-8), 121.9 (C-2 or C-3), 123.1 (C-5), 124.3 (C-3 or C-2), 170.0 (C-4b), 199.2 (C=O); MS, *m/e* 244 (M^+, 23), 163 (base), 134 (48), 119 (47), 105 (30), 91 (53), 79 (25), 77 (29), 67 (25), 55 (24).

Anal. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.40; H, 9.85.

Acknowledgment. L.M. and A.T. thank the Consiglio Nazionale delle Ricerche and the Ministero della Pubblica Istruzione for support of the work in Perugia.

Additions and Corrections

Vol. 54, 1989

Martin Newcomb,* Anne G. Glenn, and William G. Williams. Rate Constants and Arrhenius Functions for Rearrangements of the 2,2-Dimethyl-3-butenyl and (2,2-Dimethylcyclopropyl)methyl Radicals.

Page 2680, ref 18. The following should precede the citation of the review: The corresponding Grignard reagent rearrangement is known and has a half-life of ca. 30 h at 70 °C (see: Maercker, A.; Guthlein, P.; Wittmayr, H. *Angew. Chem.* **1973**, *85*, 823), and cyclization of a lithium species related to **16** occurs in days at −60 °C (see: Maercker, A.; Bsata, M.; Buchmeier, W.; Engelen, B. *Chem. Ber.* **1984**, *117*, 2547). We regret the oversight of these references.

E. M. Y. Quinga, T. Bieker, M. P. Dziobak, and G. D. Mendenhall*. Ambident Nucleophilicity of Silver Hyponitrite toward Organic Halides.

Page 2770, ref 5. A compound $Ph_2CHON{=}N(O)CHPh_2$ was reported by Francis A. Carey and co-workers: Carey, F. A.; Haynes, L. J. *J. Am. Chem. Soc.* **1970**, *92*, 7613; *J. Org. Chem.* **1973**, *38*, 3107. The spectral data in these papers agree fairly well with our data for a compound assigned the same structure, but the reported melting points differ by 15–16 °C. Different geometrical isomers may be involved. We are grateful to Professor Carey for bringing his work to our attention.

Qing-Yun Chen* and Sheng-Wen Wu. Perfluoro- and Polyfluorosulfonic Acids. 21. Synthesis of Difluoromethyl Esters Using Fluorosulfonyldifluoroacetic Acid as a Difluorocarbene Precursor.

Page 3025. Compound **15** should be $(i\text{-}C_8H_{17}O)_2P(O)OCF_2H$, not $(i\text{-}C_8H_{17}O)_2P(O)CF_2H$.

Page 3026, line 19. The last formula the CF_2H should be changed to a OCF_2H(group).

Experimental Section: add "**5j**: mp 64–66 °C. Found: C, 31.94; H, 1.61; F, 13.01; I, 42.81. $C_8H_5O_2F_2I$ requires C, 32.23; H, 1.69; F, 12.75; I, 42.60. ν_{max} (KCl pellet): 3090, 1760, 1640, 1500, 1420, 1260, 1040–1160, 860. MS: *m/e* (rel intensity) 298 (89.06), 231 (10), 203 (32.23), 127 (5.15), 104 (11.15), 51 (28.44). ^1H NMR, δ 7.63 (s, 4 H), 7.03 (t, 1 H). ^{19}F NMR: δ 12.3 (d, $J_{H\text{-}F} = 69$)." and the original numbers **5j**, **5k**, and **5l** should be changed to **5k**, **5l**, and **5m** subsequently, and all the data need not be changed.

Maria D. Rozwadowska and Arnold Brossi*. Optically Active Tetrahydro-α-phenyl-6,7-dimethoxyisoquinoline-1-methanols from (1-Phenylethyl)ureas. Absolute Configuration of (−)- and (+)-Isomers of the Erythro Series.

Page 3204. Compounds **8a,b** and compound (−)-**9**·HCl are 1-benzyl-substituted tetrahydroisoquinolines, not 1-benzoyl-substituted congeners. The correct names for these compounds should read as follows: (1*S*)- and (1*R*)-1,2,3,4-tetrahydro-1-benzyl-6,7-dimethoxy-2-[((*R*)-1-phenylethyl)carbamoyl]isoquinoline (**8a,b**) and (−)-(1*R*)-1,2,3,4-tetrahydro-1-benzyl-6,7-dimethoxyisoquinoline Hydrochloride ((−)-**9**·HCl).

Kevin E. O'Shea and Christopher S. Foote*. Quantitative Rearrangement of Monocyclic Endoperoxides to Furans Catalyzed by Co(II).

Page 3475. We failed to cite the paper by Turner, J. A.; Herz, W. *J. Org. Chem.* **1977**, *42*, 1900–1904, which reports the very similar Fe(II)-induced rearrangement of unsaturated endoperoxides derived from butadienes, a procedure for synthesis of 3-alkyl furans. We apologize for this omission.