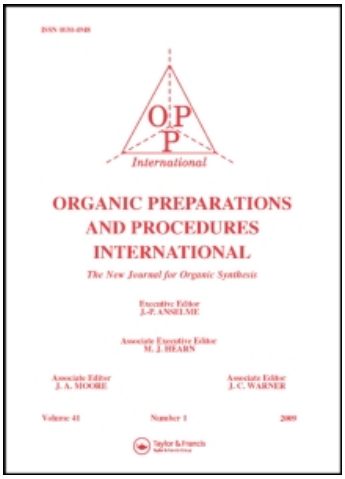


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

INVERSE-ELECTRON DEMAND DIELS-ALDER CYCLOCONDENSATIONS IN THE SYNTHESIS OF 5-8-5 FUSED RING SYSTEMS

J. Gabriel Garcia[ab]; Mark L. McLaughlin[a]
[a] Department of Chemistry, Louisiana State University, Baton Rouge, LA, USA [b] Department of Chemistry, University of Vermont, Burlington, VT

To cite this Article Garcia, J. Gabriel and McLaughlin, Mark L.(1995) 'INVERSE-ELECTRON DEMAND DIELS-ALDER CYCLOCONDENSATIONS IN THE SYNTHESIS OF 5-8-5 FUSED RING SYSTEMS', Organic Preparations and Procedures International, 27: 1, 92 — 95
To link to this Article: DOI: 10.1080/00304949509458183
URL: http://dx.doi.org/10.1080/00304949509458183

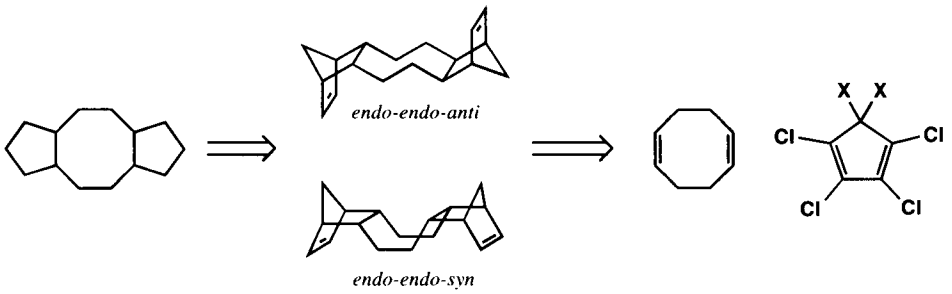
INVERSE-ELECTRON DEMAND DIELS-ALDER CYCLOCONDENSATIONS IN THE SYNTHESIS OF 5-8-5 FUSED RING SYSTEMS

Submitted by (02/07/94)

J. Gabriel Garcia*† and Mark L. McLaughlin

Department of Chemistry, Louisiana State University
Baton Rouge, LA 70803-1804, USA

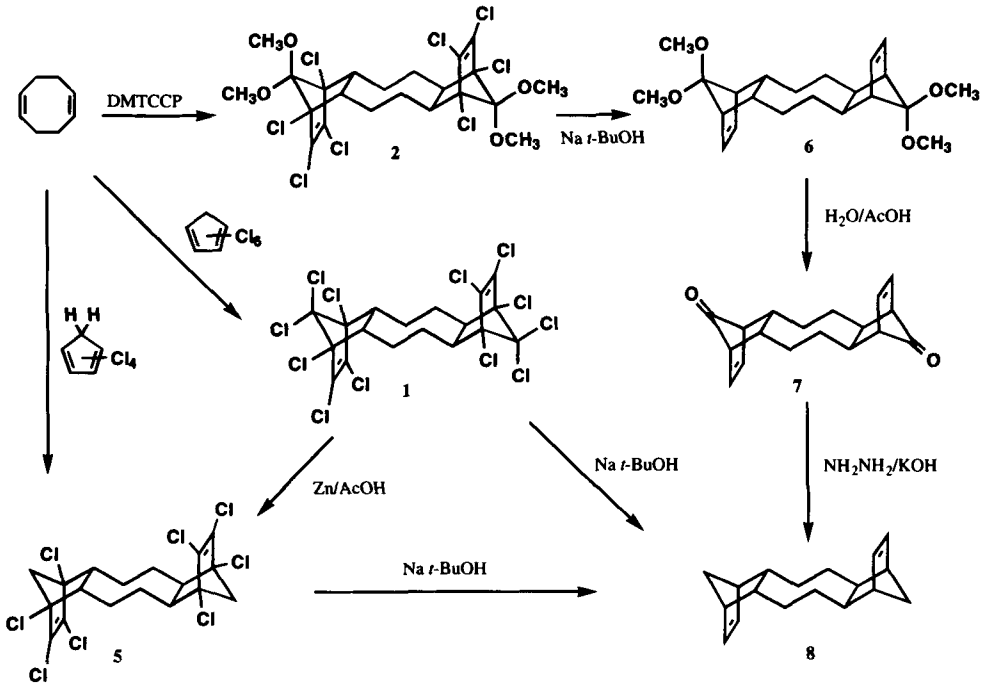
Tandem inverse-electron-demand Diels-Alder reactions of polyfunctional dienophiles have not been widely exploited for synthesis.[1] This approach potentially allows the transformation of "unactivated" olefins into cyclopentadienes as shown below for 1,5-cyclooctadiene (COD). We recently described[2,3] that a conformation-dependent transmission of π -σ-π electronic interactions influences the stereoselectivity of reverse-electron demand Diels-Alder cycloaddition between COD and electron-deficient dienes. Two different stereoisomers, *endo-endo-anti* and *endo-endo-syn*,[2,3] are obtained in a 4:1 ratio, respectively. These Diels-Alder diadducts potentially lead to the synthesis of *anti* and *syn* 5-8-5 fused-ring systems as shown below. Synthesis of pentacyclic hydrocarbon **8**, was approached by three different Diels-Alder cyclocondensations of COD, with hexachlorocyclopentadiene (HCCP), 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene (DMTCCP) and 1,2,3,4-tetrachlorocyclopentadiene (TCCP).



Diels-Alder cyclocondensation reaction of COD with HCCP and DMTCCP afforded a 4:1 mixture of the corresponding *anti* and *syn* diadducts[4] **1**, **3** and **2**, **4** in 95% and 81% yield, respectively. COD reacted with TCCP affording a 4:1 mixture of the corresponding *anti* and *syn* diadducts in only 36% yield.

Complete reduction of the dodecachlorinated compound **1** with sodium in *t*-butanol afforded **8** in poor yield (1 to 5%). Partial reduction of **1** to the corresponding octachlorinated compound **5**[5] with zinc in acetic acid was only achieved in 5% yield. However, complete reduction of **5** to the corresponding pentacyclic hydrocarbon **8** with sodium in *t*-butanol gave a better than 22% yield. The overall yields from **1** or **5** is less than 8% yield. These results led us to test for the synthetic route involving COD and DMTCCP.

Compound **2** was reduced with sodium in *t*-butanol to the corresponding tetramethoxypentacyclic compound **6**[4] in 40% yield. Acid hydrolysis of compound **6** afforded the corresponding



pentacyclic diketone (**7**)[6] in 93% yield. Wolff-Kishner reduction of **7** gave the corresponding pentacyclic hydrocarbon **8** in 60% yield, the overall yield was 18%.

EXPERIMENTAL SECTION

Melting points were determined on an electrothermal apparatus and are uncorrected. ^{1}H and ^{13}C NMR were recorded on a Bruker WP-200MHz spectrometer with chemical shifts (δ) given in ppm from internal TMS reference (in $CDCl_3$). Infrared spectra were taken on an IBM FTIR model IR-44 spectrometer. Microanalysis were performed by UC Berkeley microanalytical laboratory. Hexachlorocyclopentadiene was purchased from Aldrich Chemical Co. 5,5-Dimethoxy-1,2,3,4-tetrachlorocyclopentadiene and 1,2,3,4-tetrachlorocyclopentadiene were prepared according to literature procedure, respectively.[7,8] *endo-endo-anti*-1,6,7,8,9,14,15,16-Octachloro-17,17,18,18-tetramethoxypentacyclo-[12.2.1.$1^{6,9}$.$0^{2,13}$.$0^{5,10}$]octadeca-7,15-diene (**1**), *endo-endo-anti*-1,6,7,8,9,14,15,16,17,17,18,18-dodecachloropentacyclo[12.2.1.$1^{6,9}$.$0^{2,13}$.$0^{5,10}$]octadeca-7,15-diene (**2**), *endo-endo-syn*-1,6,7,8,9,14,15,16-Octachloro-17,17,18,18-tetramethoxypentacyclo[12.2.1.$1^{6,9}$.$0^{2,13}$.$0^{5,10}$]octadeca-7,15-diene (**3**) and *endo-endo-syn*-1,6,7,8,9,14,15,16,17,17,18,18-dodecachloropentacyclo[12.2.1.$1^{6,9}$.$0^{2,13}$.$0^{5,10}$]-octadeca-7,15-diene (**4**) are described in the literature.[2]

***endo-endo-anti*-1,6,7,8,9,14,15,16-octachloropentacyclo[12.2.1.$1^{6,9}$.$0^{2,13}$.$0^{5,10}$]octadeca-7,15-diene (5).**- A neat solution of 1,2,3,4-tetrachlorocyclopentadiene (2g, 9.8 mmol) with 1,5-cyclooctadiene (265 mg, 2.5 mmol) was slowly heated (oil bath) under continuous stirring and argon atmosphere to 130° and allowed to stir for 3 hrs. The resulting paste was cooled to 0° and the solid collected was washed with hexane followed by cold ether to give 460 mg (36%) of white solid, mp. 312-315 (dec.).

^{1}H NMR: δ 2.64 (d, 4H), 2.44 (d, 2H), 2.40 (d, 2H), 2.21 (d, 4H), 0.80 (t, 4H). ^{13}C NMR: δ 132.1, 66.4, 63.2, 55.4, 23.0. FT-IR: 2941, 2906, 1591, 1291, 1470, 1227, 1126, 1038, 944. HRMS: (Calcd., Obsd.) $C_{18}H_{16}{}^{35}Cl_7{}^{37}Cl$ (513.8733, 513.8726), $C_{18}H_{16}{}^{35}Cl_6{}^{37}Cl_2$ (515.8703, 515.8695).

Anal. Calcd. for $C_{18}H_{16}Cl_8$: C, 42.20; H, 3.15. Found: C, 42.48; H, 3.17

***endo-endo-anti*-17,17,18,18-tetramethoxypentacyclo[12.2.1.1^{6,9}.0^{2,13}.0^{5,10}]octadeca-7,15-diene (6)**.- A mixture of sodium metal (24 g, 1 mol) in dry THF (120 mL) and *t*-butanol (25 mL) was refluxed with mechanical stirring under argon atmosphere. A solution of **2** (20 g, 31 mmol) in dry THF (80 mL) was slowly added over a period of 1.5 hr. The resulting mixture was refluxed for 36 hrs, cooled to r.t. and filtered through a wire screen. The resulting dark filtrate was mixed with ice and ether (300 mL). The organic layer was washed with brine, dried over magnesium sulfate and concentrated under reduced pressure to give 4.7 g (42%) of a pale yellow solid. mp. 239-242°. ^{1}H NMR: δ 6.04 (t, 4H), 3.19 (s, 6H), 3.09 (s, 6H), 2.64 (broad s, 4H), 2.32 (d, 4H), 1.58 (d, 4H), 0.95 (t, 4H). ^{13}C NMR: δ 132.4, 117.8, 52.2, 51.6, 49.7, 43.0, 27.6. FT-IR: 2972, 2933, 2925, 2861, 2827, 1470, 1296, 1288. HRMS: (Calcd., Obsd.) $C_{22}H_{32}O_4$ (360.2310, 360.2296), $^{13}CC_{21}H_{32}O_4$ (361.2328, 361.2337), $C_{21}H_{29}O_4$ (345.2051, 345.2062), $C_{21}H_{29}O_3$ (329.2113, 329.2117), $C_{20}H_{25}O_3$ (313.1796, 313.1808), $C_7H_{11}O_2$ (127.0775, 127.0757), C_8H_9 (105.0722, 105.0702).

Anal. Calcd. for $C_{22}H_{32}$: C, 73.30; H, 8.95. Found: C, 73.52; H, 8.90

***endo-endo-anti*-17,18-dioxopentacyclo[12.2.1.1^{6,9}.0^{2,13}.0^{5,10}]octadeca-7,15-diene (7)**.- A solution of water (15 mL) in glacial acetic acid (60 mL) was warmed to 50-60°. **6** was slowly added (2.5 g, 6.9 mmol). The resulting solution was allowed to stir at that temperature for 2 hrs, cooled and filtered to give 1.6 g (87%) of a pale yellow powder, mp 224-226°. ^{1}H NMR: δ 6.43 (t, 4H), 2.78 (t, 4H), 2.42 (d, 4H), 1.71 (d, 4H), 1.10 (t, 4H). ^{13}C NMR: δ 205.3, 131.4, 54.8, 41.2, 26.4. FT-IR: 2987, 2935, 1787, 1468, 1330, 1210, 1131. HRMS: (Calcd., Obsd.) $C_{17}H_{20}O$ (240.1515, 240.1514), $C_{16}H_{20}$ (212.1571, 212.1563), $^{13}CC_{16}H_{20}$ (213.1504, 213.1600), $C_{15}H_{17}$ (197.1351, 197.1325), $^{13}CC_{14}H_{17}$ (198.1358, 198.1365), $C_{14}H_{15}$ (183.1183, 183.1171), $C_{11}H_{11}$ (143.0858, 143.0861), $C_{10}H_9$ (129.0727, 129.0701).

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.71; H, 7.61

***endo-endo-anti*-17,18-Pentacyclo[12.2.1.1^{6,9}.0^{2,13}.0^{5,10}]octadeca-7,15-diene (8)**.- A mixture of **7** (1.3 g, 4.9 mmol), hydrazine monohydrate (0.6 mL, 12 mmol) and potassium hydroxide (1.6 g, 29 mmol) in diethylene glycol (15 mL) was refluxed for 1hr. The resulting mixture of solids was extracted with ether. The combined organic layers were washed with water, brine, dried over magnesium sulfate, filtered and concentrated under reduced pressure to give 0.73 g (62%) of a pale yellow powder, mp. 124-127°. ^{1}H NMR: δ 6.01 (t, 4H), 2.58 (t, 4H), 2.07 (d, 4H), 1.61 (d, 4H), 1.25 (d, 2H), 1.23 (d, 2H). ^{13}C NMR: δ 135.0, 50.1, 49.3, 45.4, 29.0. FT-IR: 2960, 2910, 2884, 2856, 1203, 1100. HRMS: (Calcd., Obsd.) $C_{18}H_{24}$ (240.1898, 240.1871), $^{13}CC_{17}H_{24}$ (241.1938, 241.1903), $C_{13}H_{18}$ (174.1412, 174.1408), $C_{10}H_{12}$ (132.0948, 132.0938), C_8H_{11} (107.0893, 107.0857).

REFERENCES

† Present Address: Department of Chemistry, University of Vermont, Burlington, VT 05405-0125.

1. W.-D. Fessner, G. Sedelmeier, P. R. Spurr, G. Rihs and H. J. Prinzbach, *J. Am. Chem. Soc.*, **109**, 4626 (1987); b) G.I. Fray and D. P. S. Smith, *J. Chem. Soc. C*, 2710 (**1969**).
2. J. G. Garcia, F. R. Fronczek and M. L. McLaughlin, *Tetrahedron Lett.*, **32**, 3289 (1991).
3. J. G. Garcia and M. L. McLaughlin, *ibid.*, **32**, 3293 (1991).
4. refs. 2 and 3.; J. G. Garcia, F. R. Fronczek and M. L. McLaughlin, *Acta Cryst.*, **C47**, 206 (1991).
5. Crystal structure: J. G. Garcia, F. R. Fronczek and M. L. McLaughlin, *ibid.*, **C47**, 451 (1991).
6. Crystal structure: J. G. Garcia, F. R. Fronczek and M. L. McLaughlin, *ibid.*, **C47**, 2009 (1991).
7. a) J. S. Newcomer and E. T. McBee, *J. Am. Chem. Soc.*, **79**, 946 (1949); b) E. T. McBee, D. L. Crain, L. R. Belohlav and H. P. Braendlin, *ibid.*, **84**, 3557 (1962).
8. H. Roedig and L. Hörnig, *Chem. Ber.*, **88**, 2007 (1955).

****

TRANSFORMATION OF CARBOXYLIC ESTERS TO ALDEHYDES WITH SODIUM *tris*(DIETHYLAMINO)ALUMINUM HYDRIDE

Submitted by (02/07/94) Jin Soon Cha*, Jong Mi Kim, Min Kyoo Jeoung, Oh Oun Kwon and Eun Ju Kim

Department of Chemistry, Yeungnam University
Kyongsan 712-749, REPUBLIC OF KOREA

The conversion of carboxylic esters into aldehydes is important in organic synthesis. A number of useful reducing agents for such a transformation have been reported, e.g., lithium tri-*tert*-butoxyaluminum hydride,[1] diisobutylaluminum hydride,[2] sodium diisobutylaluminum hydride,[3] *bis*(4-methyl-1-piperazinyl)aluminum hydride,[4] and sodium diethylpiperidinylaluminum hydride.[5] Recently, we reported that lithium *tris*(diethylamino)aluminum hydride (LTDEA), prepared from the reaction of three equivalents of diethylamine with lithium aluminum hydride, reduces carboxylic esters to aldehydes in good yields at -78°.[6] Similarly, we synthesized the diethylamino substituted derivative of sodium aluminum hydride and applied it for conversion of carboxylic esters to aldehy-