Notes

Germacranolides of *Inula eupatorioides*. 2. Absolute Configuration of the Ineupatorolides[1,2]

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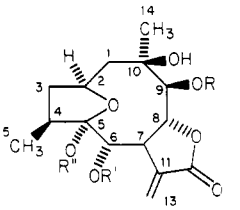
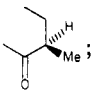
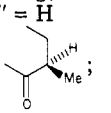
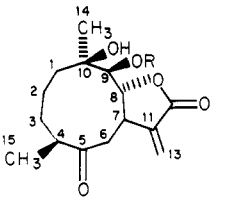
Received August 21, 1981

In an earlier article on lactone constituents of *Inula eupatorioides* L. relative configurations **1a**, **2a**, and **2b** were established for the new germacranolides ineupatolide, ineupatorolide A, and ineupatorolide B.[3] Application to ineupatolide of the empirical rules usually employed for deducing the absolute configurations of sesquiterpene lactones gave contradictory results which on balance favored absolute configuration **1a**. On the other hand, application of the rules to the ineupatorolides led to their formulation as mirror images of **2a,b** (enantiomeric to the presumed absolute configuration **1a** of ineupatolide) which may be rewritten as **3a,b** to conform with the rule that H-7 in sesquiterpenes formed in higher plants is generally α.[4]

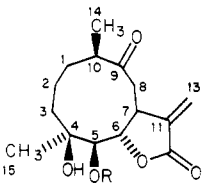
The possible occurrence of "enantiomerically related" sesquiterpene lactones in the same species seemed sufficiently unusual to require confirmation by crystallographic methods. We have therefore reisolated ineupatolide and the mixture of ineupatorolides. While we have so far been unable to prepare a suitable heavy atom derivative of **1a**, epoxyineupatorolide B1 (**3e**) gave a crystalline bromohydrin whose analysis by the anomalous dispersion method led to absolute configuration **3f**, thus verifying **3a,b** as the absolute configuration of the ineupatorolides. Crystal data for **3f** are listed in the Experimental Section. Figure 1a is a stereoscopic drawing of the molecule which represents the correct absolute stereochemistry; Figure 1b shows the atom framework. Tables I–V listing final atomic and final anisotropic thermal parameters, bond lengths, bond angles, and selected torsion angles are available as supplementary material; Tables III–V also include bond lengths, bond angles, and torsion angles of **3e** (equivalent to **2c** of ref 2 after inversion and renumbering). These show that conformations of the germacrane and lactone rings of **3e** and **3f** do not differ greatly.

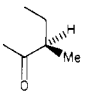
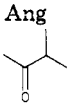
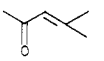
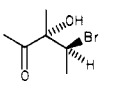


1a, R =  ;
R′ = Ang; R″ = H
b, R = R′ = Ang; R″ = H
c, R = R′ = Ang; R″ = Ac
d, R = Epoxang; R′ = Ang; R″ = H
e, R = Ang; R′ = Epoxang; R″ = H
f, R =  ;
R′ = Epoxang; R″ = H



2a, R = 
b, R = Ang



3a, R = 
b, R = Ang
c, R = 
d, R = 
e, R = 
f, R = 

(1) Dedicated to the memory of Willy Leimgruber, deceased July 8, 1981.

(2) Work at the Florida State University supported in part by a grant from the U.S. Public Health Service (CA-13121) through the National Cancer Institute.

(3) Baruah, R. N.; Sharma, R. P.; Thyagarajan, G.; Herz, W.; Govindan, S. V.; Blount, J. F. *J. Org. Chem.* **1980**, *45*, 4838.

(4) However, this requires renumbering of the carbon skeleton. Interestingly enough, ineupatolide and the ineupatorolides are compounds whose representation in two dimensions cannot be handled by the standard convention,[5] their functionalization being such that a distinction between the α and β faces by any of the criteria proposed in ref 4 is impossible. Hence depiction of the ineupatorolides as **2a,b** or **3a,b** prior to knowledge of their absolute configurations is equally satisfactory. Absolute configuration **1a** is essentially enantiomeric with **3a** if the positions of the glycol and ketone functions relative to the lactone ring are used as a criterion.

(5) Rogers, D.; Moss, G. P.; Neidle, S. J. *J. Chem. Soc., Chem. Commun.* **1972**, 142.

Three new minor sesquiterpene lactone constituents of *I. eupatorioides* were also found. Two of these were an inseparable mixture of the isobutyryl ester **3c** as major and the senecioyl ester **3d** as minor component. The structures were apparent from the ^{1}H NMR and mass spectra and were confirmed by hydrolysis of the mixture to **4a**[2] and acetylation of the latter to **4b**. A third new substance was the angelyl ester **1b** as indicated by the ^{1}H NMR and mass spectra and by acetylation to **1c**. This was confirmed by catalytic hydrogenation of **1b** to a dihydro derivative **5a** and a hexahydro derivative **5b**. The latter was identical

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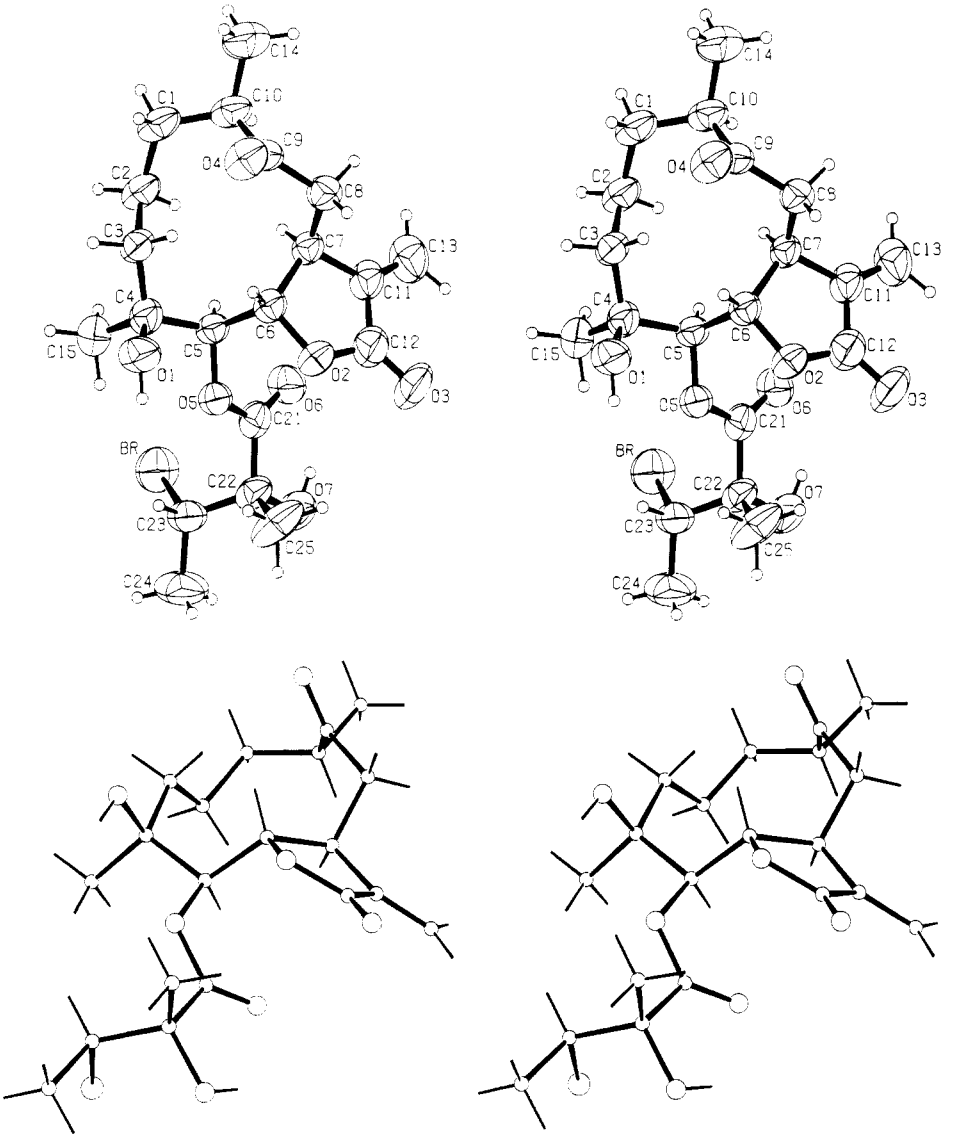
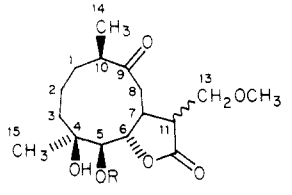
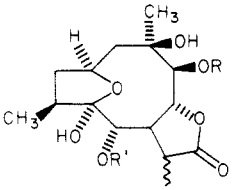


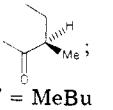
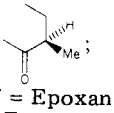
Figure 1. Top: Stereoscopic view of **3f** with ellipsoids of thermal motion. Bottom: Side view of molecular framework.

in all respects with a substance prepared by catalytic hydrogenation of ineupatolide (**1a**).



4a, R = H
b, R = Ac



5a, R = R′ = Ang
b, R = 
R′ = MeBu
c, R = 
R′ = Epoxang
d, R = Epoxang;
R′ = MeBu

Epoxidation of **1b** gave a monoepoxide whose structure was shown to be **1d** rather than **1e** as follows. Hydrogenation of **1d** gave **5d** which differed from a substance **5c** obtained by epoxidation of **1a** to **1f** and subsequent hydrogenation.

Experimental Section

Extraction of *Inula eupatorioides*. Repetition of the extraction and purification in the manner described previously[3] gave, from 1.4 kg of *I. eupatorioides* collected on Sept 15, 1979, in the Cherapunjee area of Meghalaya, India, 7 g of crude gum which was chromatographed over 200 g of silica gel, 200-mL fractions being collected in the following order: fractions 1–10 (Bz), 11–20 (Bz–EtOAc, 9:1), 21–30 (Bz–EtOAc, 6:1), 31–40 (Bz–EtOAc, 4:1), 41–50 (Bz–EtOAc, 2:1), 51–55 (Bz–EtOAc, 1:1), 56–64 (Bz–EtOAc, 1:2), 65–70 (EtOAc), 71–75 (EtOAc–MeOH, 99:1), 75–80 (EtOAc–MeOH, 9:1). Fractions 51–55 (0.5 g) which exhibited a single spot on TLC were a mixture of ineupatorolide A (**3a**) and B (**3b**).[3] Fractions 56–60 which showed a single spot on TLC (Bz–EtOAc, 1:2) were combined to yield 80 mg of a mixture of ineupatorolide C (**3c**, major component) and ineupatorolide D (**3d**, minor component) as a gum: IR ($CHCl_3$) 3550, 1770, 1718 (br), 1650, 1700, 1080, 1030 cm^{-1}; mass spectrum, m/z 364 and 346 (M^+ and $M^+ - H_2O$ of **3d**), 352 and 334 (M^+ and $M^+ - H_2O$ of **3c**), 281 ($M^+ - C_4H_7O$ and C_5H_7O), 264 ($M^+ - C_4H_8O_2$ and $C_5H_8O_2$), 263, 246, 139, 83, 71 (base peak); NMR (270 MHz; C_6D_6, which separated signals more effectively than $CDCl_3$) δ 6.35 (d, J = 2.5 Hz) and 6.34 (d, J = 2.5 Hz, H-13a of **3d** and **3c**), 5.72 (br, H-2′ of **3d**), 5.15 (d, J = 2 Hz) and 5.13 (d, 2,h-13b of **3d** and **3c**), 4.68 (d, J = 6.5 Hz) and 4.59 (d, J = 6.5 Hz, H-5 of **3d** and **3c**), 4.53 (dd, J = 6.5 Hz, 3, H-6 of both compounds), 3.3 (m) and 3.24 (dddd, J = 11, 3, 2.5, 2 Hz, H-7), 2.50 (sept, J = 7 Hz, H-2′ of **3c**), 2.34 (m, contains H-8a), 2.04 (dd, J = 14 Hz, 3, H-8b), 2.22 (d, J = 1.5 Hz) and 1.48 (d, J = 1.5 Hz, H-4′ and H-5′ of **3d**), 1.22 (d, J = 7 Hz) and 1.11 (d, J = 7 Hz, H-3′ and H-4′ of **3c**), 0.98 and 0.93

(H-15 of **3d** and **3c**), 0.81 (d, J = 7 Hz) and 0.80 (d, J = 7 Hz, H-14 of **3d** and **3c**).

Fractions 63–68 which were a mixture of a major and a minor component (TLC) were combined (1 g). The components of the mixture were separated by preparative TLC on a 0.5 mm thick plate and running the plate 6 times, using Bz–EtOAc (6:1). The more polar major constituent (0.8 g) was identified as ineupatolide (**1a**). The less polar constituent (0.1 g) was new; recrystallization from ethyl acetate furnished **1b**: mp 178 °C; IR 3550, 1770, 1720, 1650, 1125, 1080, 1010 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 6.20 (c, H-13a and vinyl H's of two angelate groups), 5.58 (d, J = 3 Hz, H-13b), 5.14 (m, H-6 and H-9), 4.70 (dd, J = 6 Hz, 5.5, H-8), 4.35 (m, H-2), 3.85 (m, H-7), 1.92 (c, methyls of angelates), 1.35 (H-14), 1.05 (d, J = 7 Hz, H-15); mass spectrum, m/z 478 (M^+), 460 ($M^+ - H_2O$), 378 ($M^+ - C_5H_8O_2$), 360 ($M^+ - H_2O - C_5H_8O_2$), 278 ($M^+ - 2\ C_5H_8O_2$), 260 ($M^+ - H_2O - 2\ C_5H_8O_2$), 228, 83 ($C_5H_7O$).

Anal. Calcd for $C_{25}H_{34}O_9$: mol wt 478.2200. Found: mol wt (mass spectrum) 478.2194.

Hydrolysis of 3c,d. A solution of 20 mg of the **3c,d** mixture in 4 mL of MeOH and 0.5 mL of 40% aqueous NaOH was stirred in a nitrogen atmosphere, the reaction being monitored by TLC. After disappearance of all starting material the solution was diluted with H_2O, acidified with acetic acid, and extracted thoroughly with $CHCl_3$. Evaporation of the washed and dried extract yielded 18 mg of gummy material whose IR, NMR, and mass spectrum were essentially superimposable on that of crystalline **4a** from hydrolysis of the ineupatorolide A/B mixture.[3] Acetylation with acetic anhydride–pyridine followed by the usual workup afforded 12 mg of **4b** (single spot on TLC): IR 3550, 1775, 1740, 1705, 1110 cm^{-1}; mass spectrum, m/z 356 (M^+), 324 (M^+ – MeOH), 314 ($M^+ - C_2H_2O$), H_2O), 282, 262; NMR signals superimposable on those of the **4c,d** mixture[3] except for replacement of the ester side chain signals by an acetate methyl at 2.01 ppm.

Reactions of 1b. (a) Acetylation of 30 mg of **1b** with acetic anhydride–pyridine for 4 days at room temperature, workup in the usual fashion, and preparative chromatography of the crude product afforded 25 mg of gummy **1c**: IR 3500, 1770, 1750, 1725, 1650, 1130 cm^{-1}; NMR (60 MHz, $CDCl_3$) δ 6.20 (c, H-13a and vinyl H's of two angelates), 5.58 (d, J = 3 Hz, H-13b), 5.14 (d, J = 9 Hz, H-9), 5.02 (d, J = 4.5 Hz, H-6), 4.6 (c, H-2 and H-8), 3.95 (m, H-7), 2.05 (Ac), 1.95 (c, methyls of angelates), 1.36 (H-14), 1.05 (d, J = 7 Hz, H-15); mass spectrum, m/z 520 (M^+), 478 ($M^+ - H_2O$), 378 ($M^+ - C_5H_8O_2$), 278 ($M^+ - 2\ C_5H_8O_2$), 260, 160, 149, 97, 83.

Anal. Calcd for $C_{27}H_{36}O_{10}$: mol wt 520.2306. Found: mol wt (mass spectrum) 520.2300.

(b) Epoxidation of 30 mg of **1b** in 4 mL of $CHCl_3$ with 100 mg of m-chloroperbenzoic acid at 0 °C for 3 days followed by dilution with 50 mL of $CHCl_3$, washing 3 times with 50 mL of dilute $NaHSO_3$ solution and water, drying, and evaporation at reduced pressure afforded 28 mg of gummy **1d**: IR 3600, 1770, 1725, 1180, 1125, 1080 cm^{-1}; NMR (60 MHz) δ 6.21 (c, H-13a and vinyl H of angelate group), 5.56 (d, J = 3 Hz, H-13b), 5.17 (m, H-6 and H-9), 4.75 (dd, J = 6 Hz, 5.5, H-8), 4.29 (m, H-2), 3.81 (m, H-7), 3.00 (q, J = 6 Hz, H under epoxide), 2.0 (c, methyls of angelate), 1.64 and 1.45 (d, J = 7 Hz, methyls on epoxyangelate), 1.35 (H-14), 1.07 (d, J = 7 Hz, H-15); mass spectrum, m/z 494 (M^+), 479 ($M^+ - CH_3$), 394 ($M - C_5H_8O_2$), 378 ($M^+ - C_5H_8O_3$), 278, ($M^+ - C_5H_8O_2 - C_5H_8O_3$), 139, 99, 83 (base peak).

Anal. Calcd for $C_{25}H_{34}O_{10}$: mol wt 494.2150. Found: mol wt (mass spectrum) 494.2136.

(c) Hydrogenation of 15 mg of **1d** in 25 mL of EtOAc with 100 mg of 10% Pd–C for 8 h followed by filtration and evaporation of the filtrate at reduced pressure yielded **5d** as a gum: IR 3590, 1775, 1730, 1675, 1600, 1460, 1375, 1135, 1075, 935 cm^{-1}; mass spectrum, m/z 498 (M^+), 480 ($M^+ - H_2O$), 396 ($M^+ - C_5H_{10}O_2$), 380, 181, 115, 85.

(d) Hydrogenation of 50 mg of **1b** in 25 mL of EtOAc with 200 mg of 10% Pd–C for 16 h, filtration, and evaporation at reduced pressure yielded 50 mg of solid which exhibited two spots on TLC (Bz–EtOAc, 2:1). Separation by preparative TLC (Bz–EtOAc, 4:1) gave as the less polar fraction 30 mg of **5b** which crystallized on trituration with EtOAc: mp 170 °C; IR 3580, 1770, 1728, 1290, 1170, 1135, 1120, 1090, 1065, 1010, 980, 970 cm^{-1}; NMR (60 MHz) δ 5.15 (c, H-6 and H-9), 4.60 (dd, J = 6, 5.5 Hz, H-8), 4.25 (m, H-2), 1.40–0.80 (seven superimposed methyls); mass spectrum, m/z 484 (M^+), 469 ($M^+ - CH_3$), 466 ($M^+ - H_2O$), 465, 383 ($M^+ - C_5H_9O_2$), 283, 265, 102, 85 (C_5H_9O, base peak). The more polar fraction **5a**, weight 20 mg, was recrystallized from ethyl acetate: mp 158 °C; IR 3600, 1775, 1750, 1735, 1140, 960 cm^{-1}; NMR (60 MHz) δ 6.18 (c, overlapping vinyl H's of two angelates), 5.14 (m, H-6 and H-9), 4.71 (m, H-8), 3.85 (m, H-7), 4.35 (m, H-2), 1.92 (c, methyls of two angelates), 1.35 (H-14), 1.20 (d, 7, H-13), 1.05 (d, 7, H-15); mass spectrum, m/z 480 (M^+), 462 ($M^+ - H_2O$), 380 ($M^+ - C_5H_8O_2$), 362, 280, 83. A substance identical with **5b** in all respects (melting point, TLC, IR, NMR, and mass spectra) was obtained in 30 mg yield by hydrogenation of 50 mg of ineupatolide (**1a**) in 25 mL of EtOAc for 16 h with 200 mg of Pd–C followed by the usual workup.

Epoxidation of Ineupatolide. A solution of 20 mg of **1a** in 4 mL of $CHCl_3$ was stirred with 100 mg of m-chloroperbenzoic acid at room temperature for 4 h, diluted with 50 mL of $CHCl_3$, washed with dilute $NaHSO_3$ and H_2O, and dried. Evaporation gave a gum which exhibited two spots on TLC. Separation by preparative TLC gave starting material and as the more polar fraction a gummy epoxide **1f**: mass spectrum, m/z 496 (M^+), 478 ($M - H_2O$), 363 ($M^+ - H_2O - C_5H_7O_3$), 261 ($M^+ - H_2O - C_5H_7O_3 - C_5H_9O_2$), 115 ($C_5H_2O_3$, base peak. Hydrogenation of 10 mg of **1f** in 25 mL of EtOAc with 100 mg of 10% Pd–C for 2 h followed by the usual workup gave 10 mg of a gum (**5c**), whose IR spectrum and TLC behavior differed from that of **5d**: IR 3595, 1775, 1730, 1675, 1605, 1605, 1370, 1079, 1079, 930 cm^{-1}; mass spectrum, m/z 498 (M^+), 480 ($M^+ - H_2O$), 396 ($M - C_5H_{10}O_2$), 378, 365, 115, 85.

Preparation of 3f. A solution of 50 mg of **3e**[3] in 4 mL of MeOH was cooled to 5 °C and 4 drops of concentrated HBr solution was added. After 72 hr at room temperature the solution was diluted with water and extracted with $CHCl_3$. Evaporation of the washed and dried solution at reduced pressure gave a residue which showed two spots on TLC. The material responsible for the major spot was separated by preparative TLC (EtOAc–Bz, 1:2): yield 30 mg of **3f**, mp 200 °C; NMR signals (270 MHz, $CDCl_3$) δ 6.42 (d) and 5.81 (d, J = 2 Hz, H-13), 4.74 (d, J = 7 Hz, H-5), 4.58 (dd, J = 7, 3 Hz, H-6), 4.43 (q, J = 7 Hz, H-3′), 3.64 (m, H-7), 2.86 (m, H-10), 2.67 (AB system of H-8), 1.76 (d, J = 7 Hz, H-4′), 1.57 (H-5′), 1.26 (H-15), 1.13 (d, J = 7 Hz, H-14); mass spectrum, m/z 462, 460, 460 (M^+, very weak) 447, 445 ($M^+ - CH_3$), 444, 442 ($M^+ - H_2O$), 433, 431, 429, 427, 419, 417, 404, 402, 381, 363, 353, 346, 335 (353 – H_2O, M^+ 317.9) 307, 282, 264 ($M^+ - C_5H_9O_3Br$, base peak), 247, 236, 229, 218.

Anal. Calcd for $C_{20}H_{29}O_7Br^{81}$: mol wt $C_{20}H_{29}O_7Br^{79}$, 462.1076; 460.1097. Found: mol wt (mass spectrum, peak matching) 462.1078; 460.1100.

X-ray Analysis of 3f. Crystals of **3f** suitable for analysis were prepared by slow crystallization from ethyl acetate–hexane. They were orthorhombic, space group $P2_12_12_1$, with a = 10.066 (2) Å, b = 13.184 (2) Å, c = 16.675 (3) Å, and d_{calcd} = 1.385 g cm^{-3} for z = 4 ($C_{20}H_{29}BrO_7$, mol wt 461.35). The intensity data were measured on a Hilger-Watts diffractometer (Ni-filtered Cu Kα radiation, θ–20 scans, pulse-height discrimination). The size of the crystal used for data collection was approximately 0.10 × 0.20 × 0.5mm; the data were corrected for absorption (μ = 31.3 cm). A total of 1725 independent reflections were measured for θ < 57°, of which 1552 were considered to be observed [$I > 2.5\sigma(I)$]. The structure was solved by a multiple-solution procedure[6] and was refined by full-matrix least-squares methods. Three reflections which were strongly affected by extinction were excluded from the final refinement and difference map. In the final refinement, anisotropic thermal parameters were used for the nonhydrogen atoms and isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations, but their parameters were not refined. The final discrepancy indices are R = 0.038 and R_w = 0.042 for the remaining 1549 observed reflections. The final difference map has no peaks greater than ±0.5 e $Å^{-3}$.

The absolute configuration is based on the anomalous scattering of the bromine atom and was established by refining both enantiomers. The weighted R values were 0.0417 for the configuration shown and 0.0540 for its antipode. Thus, by Hamilton's

(6) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *27*, 368.

test,[7] the configuration shown corresponds to the absolute configuration.

Registry No. **1a**, 75102-66-8; **1b**, 79721-99-6; **1c**, 79722-00-2; **1d**, 79722-01-3; **1f**, 79735-20-9; **3a**, 75102-67-9; **3b**, 75102-68-0; **3c**, 79722-02-4; **3d**, 79722-03-5; **3e**, 75196-27-9; **3f**, 79722-04-6; **4a** (isomer 1), 75111-48-7; **4a** (isomer 2), 75172-29-1; **4b** (isomer 1), 79722-06-8; **4b** (isomer 2), 79722-05-7; **5a**, 79722-07-9; **5b**, 79722-08-0; **5c**, 79735-21-0; **5d**, 79735-22-1.

Supplementary Material Available: Tables listing final atomic (Table I) and final anisotropic thermal (Table II) parameters, bond lengths (Table III), bond angles (Table IV), and selected torsion angles (Table V) for **3f** (6 pages). Ordering information is given on any current masthead page.

(7) Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 506.

Deoxygenation of 7-Oxabicyclo[2.2.1]hepta-2,5-diene Systems to Substituted Benzenes by Titanium Tetrachloride–Lithium Aluminum Hydride[1]

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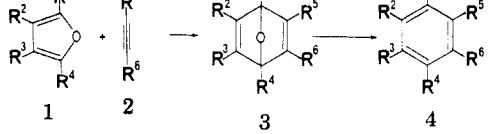
Received June 15, 1981

It is well-known that furans 1 readily undergo Diels–Alder cycloadditions with dienophiles 2 to form the oxygen-bridged six-membered carbocycles 3. The deoxygenation of 3 appears to constitute an attractive route for the construction of substituted benzenes 4.

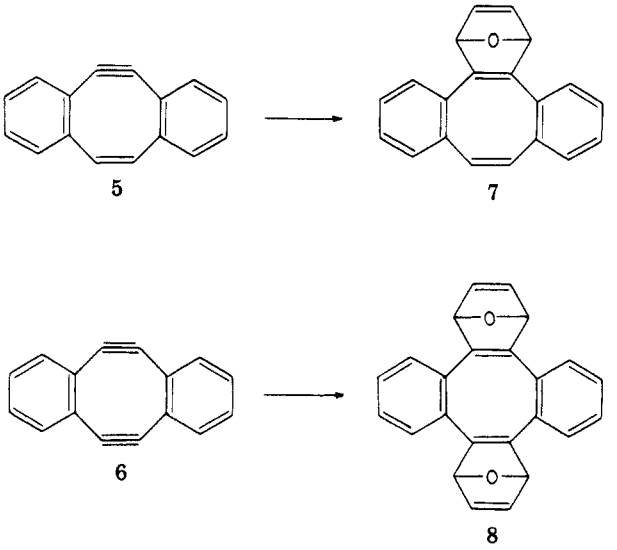


1 2 3 4

In contrast to the related cycloadditions between thiophenes and dienophiles,[3] whose adduct would subsequently expel a sulfur atom spontaneously on heating, the analogous deoxygenation process is thermodynamically less favorable. Consequently, it is important to note that thiophenes can undergo Diels–Alder reactions with only a very limited choice of dienophiles. Therefore, the utility of furans for such preparative purposes would find greater use if the final deoxygenation step can be realized synthetically.

To our best knowledge, this type of transformation has only been reported sporadically in the literature. However, the reagent used in each case is not universal for all oxygen-bridged compounds 3. For example, when 3 is fused to a pyridine ring, lithium amalgam can, in general, effect the deoxygenation.[4] On the other hand, when 3 is extensively conjugated with aromatic systems, magnesium[5] or zinc dust in hydrochloric acid[6] can help to pull off the oxygen atom. When 3 is activated by four cyano groups, the addition of triphenyl phosphine, followed by the elimination of triphenyl phosphine oxide at 195 °C, provides tetracyanobenzene.[7] Unfortunately, none of the aforementioned reagents could furnish the benzene moiety from the unactivated furan adduct 3. By far, the only viable method for this aromatization process is via a two-step procedure, i.e., catalytic hydrogenation of one of the two double bonds, followed by dehydration[8] upon treatment with acid.

We have long been interested in the cycloaddition reactions between furans and strained acetylenes, e.g., 5,6-didehydrodibenzo[*a*,*e*]cyclooctene (5) and 5,6,11,12-tetradehydrodibenzo[*a*,*e*]cyclooctene (6), from which 5,8-epoxy-5,8-dihydrotribenzo[*a*,*c*,*e*]cyclooctene (7) and 1,4,9,12-diepoxy-1,4,9,12-tetrahydrotetraphenylene (8) were isolated.[9] The compounds 7 and 8 seem to be probable precursors for the preparation of tribenzo[*a*,*c*,*e*]cyclooctene (9) and tetraphenylene (10), respectively. We have tried the single-step deoxygenation of 7 and 8 with a variety of deoxygenation reagents, e.g., triphenyl phosphine, triphenyl arsine, zinc–copper couple, and magnesium as well as zinc dust etc., without success. After some experimentation, we finally discovered that titanium tetrachloride–lithium aluminum hydride[10] was effective for such deoxygenation reactions.[11] To this end, we first chose to apply this reagent pair to three model oxygen-bridged compounds, namely, dimethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (11),[12] dimethyl 1-methyl-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (12), and dimethyl 1,4-dimethyl-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (13).[3] Thus, when the compounds 11–13 were allowed to react with a mixture of titanium tetrachloride (6.5 molar equiv), lithium aluminum hydride (2.5 molar equiv), and triethylamine (1 molar equiv) in THF for 24 h under nitrogen at room temperature and following the usual workup, the corresponding phthalates 14, 15,[13] and 16[3,12] were isolated in moderate yields.[15]



5 7 6 8

(1) Dedicated to the memory of the late Professor Franz Sondheimer.
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