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Configurations of Cycloadducts Formed in Asymmetric Intramolecular Diels–Alder Reactions

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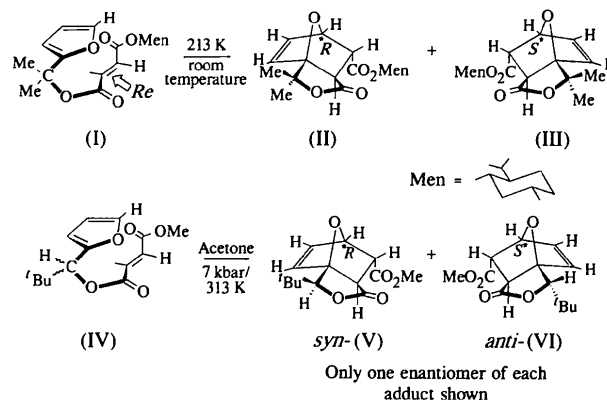
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Abstract

Intramolecular cycloaddition reactions of two furfuryl fumarates yield, after crystallization, pure diastereomers of oxabicyclo[2.2.1]heptene derivatives which are versatile starting points for the total synthesis of natural products. The crystal structures of the adducts, menthyl (3*aS*,6*R*,7*R*,7*aR*)-1,3,3*a*,6,7,7*a*-hexahydro-3,3-dimethyl-1-oxo-3*a*,6-epoxyisobenzofuran-7-carboxylate, C₂₁H₃₀O₅, and methyl *syn*-3-*tert*-butyl-1,3,3*a*,6,7,7*a*-hexahydro-1-oxo-3*a*,6-epoxyisobenzofuran-7-carboxylate, C₁₄H₁₈O₅, establish the configuration at the chiral centers and provide insights into the factors controlling the diastereomeric differentiation.

Comment

Intramolecular Diels–Alder (IMDA) reactions have been shown to be of great value in the synthesis of bicyclic and polycyclic carbocycles and heterocycles (Jalis, 1984; Taber, 1984). As part of our investigations of asymmetric induction in the IMDA reactions of furan derivatives, we have determined the structures of two adducts. Menthyl (3*aS*,6*R*,7*R*,7*aR*)-1,3,3*a*,6,7,7*a*-hexahydro-3,3-dimethyl-1-oxo-3*a*,6-epoxyisobenzofuran-7-carboxylate, (II), could be isolated in the enantiopure form from the kinetically controlled cycloaddition of the *in situ* prepared 1-(2-furyl)-1-methylethyl menthyl fumarate, (I) (Butz, 1996; Butz & Sauer, 1997). Methyl *syn*-3-*tert*-butyl-1,3,3*a*,6,7,7*a*-hexahydro-1-oxo-3*a*,6-epoxyisobenzofuran-7-carboxylate, (V), has been preferentially formed over the corresponding *anti* adduct, (VI), in the high-pressure-induced reaction of 1-(2-furyl)-2,2-dimethylpropyl methyl fumarate, (IV), under thermodynamic control. The thermally induced cyclization of (IV) has been described by Jung & Gervay (1991).



In the first case, we attempted to induce π -facial diastereo-differentiation by the attachment of a menthyl ester as a chiral auxiliary (Oppolzer, 1983; Paquette, 1984; Wurziger, 1984). The diastereoselectivity achieved, however, was very disappointing. The two possible diastereomers were obtained only in a 55:45 ratio (10% diastereomeric excess). Fortunately, the major isomer (II) can be isolated in pure form with just two crystallization steps and so it is available for further synthesis. The absolute configuration of the stereocenters in compound (II) have been derived from the known absolute configuration of menthol.

The observed molecular structure of (II) (Fig. 1) implies that the diene must have attacked from the *Si* side of the dienophile. The *Si* side, however, was expected to be shielded by the isopropyl group of the auxiliary if one assumes that the conformation of the ester bond is *syn* in the transition state (Helmchen, Karge & Weetman, 1986). Since in the crystal structure the isopropyl group points towards the tricyclic adduct, whereas the rest of the menthyl skeleton points away

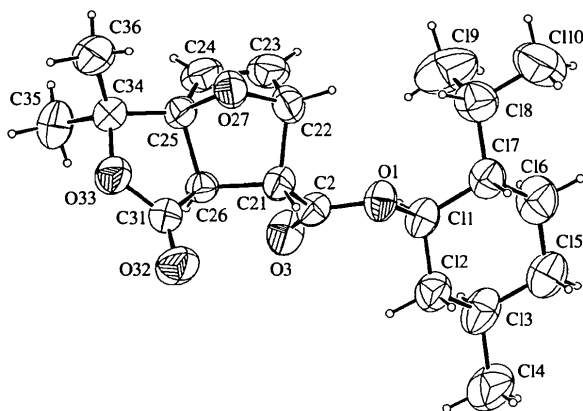


Fig. 1. The molecular structure of compound (II) showing the labeling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels and H atoms are drawn as small circles of arbitrary radii.

from it, one might argue that the rest of the menthyl skeleton may actually be bulkier than the isopropyl group. This would be in line with the observed product distribution.

In the second IMDA system, the diene attack may in principle take place either from above or below the furan plane to form the *syn*-adduct (V) or its diastereomeric *anti*-form (VI), respectively. With racemic (IV) as starting material, a 93:7 mixture of diastereomers was obtained. The major (racemic) isomer was isolated by recrystallization. The configuration could not be determined unambiguously by NMR spectroscopy (NOE). X-ray analysis unexpectedly revealed that the major product has the *syn* configuration, (V), with a pseudo-axial orientation of the *tert*-butyl group (Fig. 2). A similar IMDA system with a δ -lactone ring was reported by Woo & Keay (1994).

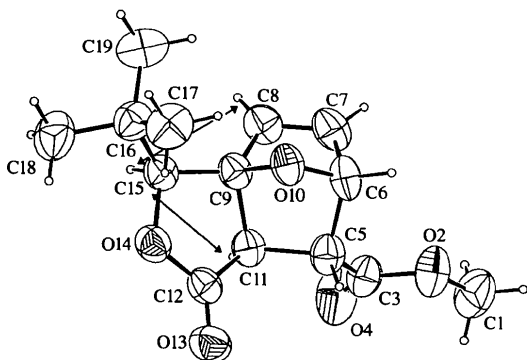


Fig. 2. The molecular structure of compound (V) showing the labeling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels and H atoms are drawn as small circles of arbitrary radii. The arrows indicate the observed NOE contacts between the H8, H11 and H15 atoms.

The position of the *tert*-butyl group results from balancing the non-bonding interactions with the oxygen bridge on the one side and with the olefinic H8 atom on the other. The torsion angles C16—C15—C9—O10 and C16—C15—C9—C8 are 47.0(2) and $-81.1(2)^\circ$, respectively. As a consequence of this, the distances H11...H15 [2.777(3) Å] and H8...H15 [2.838(2) Å] become similar. This explains the mediocre NOE signals observed for both proton pairs in the major isomer, which at first caused some confusion; we had anticipated a strong enhancement between the H11 and H15 atoms for the *syn* conformer, because the H15 atom was expected to point inside towards the H11 atom. But in fact the γ -lactone ring deviates markedly from the ideal envelope form, thus turning the H15 atom in the opposite direction outside the molecule towards the H8 atom (Fig. 2).

Experimental

For compound (II), 2-(2-furyl)-2-propanol (16 mmol) was deprotonated using sodium hydride (16 mmol, 1 equivalent) in dry THF (40 ml) at room temperature for 1 h. The THF was then evaporated and replaced by dry toluene (40 ml). The mixture was cooled below 197 K and subsequently treated with DMAP (8 mmol, 0.5 equivalents) and (+)- β -carbo-menthoxyacryloyl chloride (32 mmol, 2 equivalents, 1.6 M in toluene). After addition was complete, the red-brown mixture was kept at 203 K for 1 h and then allowed to warm slowly to room temperature over 5–6 h. The reaction was quenched by filtration through a plug of Celite, followed by extensive washing with toluene (100 ml). Evaporation of the filtrate and chromatographic workup of the residue provided a mixture of diastereomers (II) and (III). Recrystallization from methanol gave pure adduct (II) in 19% yield. For compound (V), the furfuryl fumarate (IV) (1 mmol) was dissolved in dry acetone (8 ml) saturated with argon. This solution was completely transferred into a flexible teflon tube which was stoppered at both sides by stainless steel plugs. The reaction was routinely performed at 7 kbar (1 bar = 10^5 Pa) and 313 K for 18 h in a special high-pressure apparatus (NOVA SWISS). After decompression, the solvent was removed and the residue purified by flash chromatography using mixtures of petroleum ether–ethyl acetate. Recrystallization from methanol gave the major adducts (yield 50–60%) within two steps.

Compound (II)

Crystal data

C₂₁H₃₀O₅

$M_r = 362.47$

Orthorhombic

$P2_12_12_1$

$a = 7.4918(7)$ Å

$b = 11.3118(13)$ Å

$c = 24.245(3)$ Å

$V = 2054.7(4)$ Å³

$Z = 4$

$D_x = 1.172$ Mg m⁻³

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71069$ Å

Cell parameters from

1790 reflections with

$I/I(\sigma) > 20$

$\theta = 2.46$ – 23.80°

$\mu = 0.08$ mm⁻¹

$T = 293(2)$ K

Needle

$0.75 \times 0.15 \times 0.12$ mm

Colourless

Data collection

Stoe IPDS diffractometer $R_{\text{int}} = 0.0625$
 Rotation scans $\theta_{\text{max}} = 23.8^\circ$
 Absorption correction: none $h = -8 \rightarrow 7$
 10 118 measured reflections $k = -12 \rightarrow 12$
 3101 independent reflections $l = -27 \rightarrow 27$
 2485 reflections with
 $I > 2\sigma(I)$

Refinement

Refinement on F^2 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $R = 0.0367$ $\Delta\rho_{\text{max}} = 0.10 \text{ e } \text{\AA}^{-3}$
 $wR = 0.0821$ $\Delta\rho_{\text{min}} = -0.11 \text{ e } \text{\AA}^{-3}$
 $S = 1.075$ Extinction correction: none
 3101 reflections Scattering factors from
 240 parameters *International Tables for*
 H atoms riding *Crystallography* (Vol. C)
 $w = 1/[\sigma^2(F_o^2) + (0.0454P)^2$
 $+ 0.023P]$
 where $P = (F_o^2 + 2F_c^2)/3$

Compound (V)**Crystal data**

$\text{C}_{14}\text{H}_{18}\text{O}_5$ Mo $K\alpha$ radiation
 $M_r = 266.29$ $\lambda = 0.71069 \text{ \AA}$
 Triclinic Cell parameters from
 $P\bar{1}$ 1736 reflections with
 $a = 7.7300 (10) \text{ \AA}$ $l\sigma(I) > 12$
 $b = 9.4267 (10) \text{ \AA}$ $\theta = 2.28\text{--}24.69^\circ$
 $c = 9.9854 (10) \text{ \AA}$ $\mu = 0.10 \text{ mm}^{-1}$
 $\alpha = 79.235 (8)^\circ$ $T = 293 (2) \text{ K}$
 $\beta = 88.902 (10)^\circ$ Prism
 $\gamma = 75.125 (9)^\circ$ $0.46 \times 0.40 \times 0.15 \text{ mm}$
 $V = 690.54 (14) \text{ \AA}^3$ Colourless
 $Z = 2$
 $D_x = 1.281 \text{ Mg m}^{-3}$
 D_m not measured

Data collection

Stoe IPDS diffractometer $R_{\text{int}} = 0.0273$
 Rotation scans $\theta_{\text{max}} = 24.69^\circ$
 Absorption correction: none $h = -8 \rightarrow 9$
 4199 measured reflections $k = -10 \rightarrow 10$
 2159 independent reflections $l = -11 \rightarrow 11$
 1792 reflections with
 $I > 2\sigma(I)$

Refinement

Refinement on F^2 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $R = 0.0402$ $\Delta\rho_{\text{max}} = 0.15 \text{ e } \text{\AA}^{-3}$
 $wR = 0.1130$ $\Delta\rho_{\text{min}} = -0.13 \text{ e } \text{\AA}^{-3}$
 $S = 1.123$ Extinction correction: none
 2159 reflections Scattering factors from
 176 parameters *International Tables for*
 H atoms riding *Crystallography* (Vol. C)
 $w = 1/[\sigma^2(F_o^2) + (0.0653P)^2$
 $+ 0.0961P]$
 where $P = (F_o^2 + 2F_c^2)/3$

For both compounds, data collection: *EXPOSE* (Stoe & Cie, 1996); cell refinement: *CELL* (Stoe & Cie, 1996); data re-

duction: *INTEGRATE* (Stoe & Cie, 1996); program(s) used to solve structures: *SIR92* (Altomare, Cascarano, Giacovazzo & Guagliardi, 1993); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *PLATON* (Spek, 1990); software used to prepare material for publication: *PLATON* and *SHELXL93*.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BM1116). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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4-(9-Fluorenoxy)-2-phenylphthalazin-1(2H)-one

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Abstract

The title compound, $\text{C}_{27}\text{H}_{18}\text{N}_2\text{O}_2$, was prepared from the reaction of the ambidentate anion of 2-phenyl-1,2,3,4-tetrahydrophthalazine-1,4-dione with 9-bromo-