Dimethyldioxirane Oxidation of Exocyclic (E,E)-Cinnamylideneketones*

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Exocyclic (E,E)-cinnamylideneketones were oxidized by an excess of isolated dimethyldioxirane (DMDO, in acetone solution) at room temperature, providing diastereomeric mixtures of the α,β;γ,δ-diepoxides. In the case of derivatives bearing an ortho-nitrocinamylidene moiety, α,β-monoepoxides were also isolated as minor products. The structures of all new compounds and the stereochemistry of the monoepoxides and diepoxide diastereomers were established by NMR studies.

Introduction

(E,E)-Cinnamylideneacetophenones (1,5-diphenyl-2,4-pentadien-1-ones) are well known α,β;γ,δ-unsaturated ketones. Certain of their bromoderivatives have been seen as excellent candidates to design effective second-order non-linear optical materials,[1] whereas other cinnamylideneketones exerted significant antiproliferative effects on multiresistant cancer cell lines.[2] Despite the scarce number of potential biological or industrial applications of cinnamylideneacetophenones, these compounds have been widely used as starting materials for the synthesis of various heterocyclic compounds, such as 2-styryl-1,5-benzothiazepines,[3] styryl-chromones,[4] and styrylpyrazoles,[5] 2-benzoyl-1,5-diphenylpyrroles,[6] 2-styrylchromones,[7] and 3-styrylchromones.[8] Previously, we also investigated the epoxidation of (E,E)-cinnamylideneacetophenones with different oxidizing agents.[8,9] When isolated dimethyldioxirane was used as oxidant, diastereomeric mixtures of α,β;γ,δ-diepoxides were obtained, in some cases together with α,β-monoepoxides as minor by-products. When (E,E)-2′-hydroxycinnamylideneacetophenones were oxidized under the same reaction conditions, 2′-hydroxy-γ,δ-epoxycinnamylideneacetophenones could also be detected and isolated.[8] Hydrogen peroxide or iodosylbenzene in combination with Jacobsen’s salen MnIII catalyst have also been used; in such cases, diastereomeric mixtures of α,β;γ,δ-diepoxides and also γ,δ-monoepoxides were formed. It is worth mentioning that the Julia asymmetric epoxidation procedure has provided α,β-monoepoxides in one case.[10]

The related exocyclic α,β,γ,δ-unsaturated ketone have hitherto received less attention and the synthesis of their few representatives has been described in the literature.[11] For this reason, as a continuation of our work on (E,E)-cinnamylideneacetophenones, we have undertaken studies on the synthesis and chemical transformations of such dienones. In our present paper, the synthesis and dimethyldioxirane epoxidation of exocyclic α,β,γ,δ-unsaturated ketones are reported. We have decided to investigate the influence of various structural elements of the exocyclic α,β,γ,δ-unsaturated ketones used, namely the size of the benzocyclanone ring and the influence of an ortho-substituent in the cinnamylidene moiety, because this substituent is in the vicinity of one of the two double bonds to be epoxidized.

Results and Discussion

Synthesis

The benzocyclanones 3a–i were synthesized by the base-catalyzed condensation of 1-indanone 1a, 1-tetralone 1b, and 1-benzosuberone 1c with cinnamaldehydes 2a–e to afford the appropriate dienones (Scheme 1). The (E,E)-benzocyclanones 3a,d,e,g are known compounds,[11] whereas (E,E)-cinnamylideneketones 3b,c,f,h,i are new compounds and were obtained in very good yields (72–86%).

Isolated dimethyldioxirane proved to be a convenient oxidant for the stereoselective epoxidation of a wide variety of exocyclic α,β-unsaturated ketones.[12] This versatile oxidant was beneficially used for the preparation of the α,β,γ,δ-diepoxides of (E,E)-cinnamylideneacetophenones.[8] On the basis of all these experiences, dimethyldioxirane was considered for the epoxidation of exocyclic α,β,γ,δ-unsaturated ketones 3a–i (Scheme 2).

* Dedicated to Professor Dr Branko Stanovnik on the occasion of his 70th birthday.
(E,E)-2-Cinnamylidene-1-indanones (3a–c), (E,E)-2-cinnamylidene-1-tetralones (3d–f) and (E,E)-2-cinnamylidene-1-benzosuberones (3g–i) were allowed to react with one molar equivalent of isolated dimethyldioxirane in acetone (0.07–0.10 M)\(^{[13]}\) at room temperature and the progress of the reaction was monitored by TLC. After a 24-h reaction time, the two main components in the reaction mixture were the starting material and the appropriate \(\alpha,\beta,\gamma,\delta\)-diepoxide, accompanied by several by-products. Another molar equivalent of dimethyldioxirane was added to the reaction mixture each day until the complete conversion of the starting material (cf. Experimental). Except for the nitro-substituted dienones 3c,f,i, only \(\alpha,\beta,\gamma,\delta\)-diepoxides 4a,b,d,e,g,h were isolated after the complete conversion of the starting dienones. The presence of an ortho-nitro group considerably slowed down the reaction and a complete conversion of the starting material required a higher amount of oxidant and much longer reaction times (cf. Experimental). In these cases, \(\alpha,\beta\)-monooxepides 5a–c were first detected by NMR spectroscopy and then isolated by preparative TLC.

Based on our experimental results, it can be concluded that the ring size of the benzocyclanone ring and the ortho-methoxy substituent in the cinnamylidene moiety of the starting material have no influence on this epoxidation reaction. In the case of the unsubstituted and methoxysubstituted compounds, no difference was observed in the reactivity of the two double bonds under the reaction conditions used. However, the ortho-nitro group considerably reduced the reactivity of the \(\gamma,\delta\)-double bond to the electrophilic oxidant dimethyldioxirane (DMDO), giving rise to the formation of \(\alpha,\beta\)-monooxepides. These results agreed with those obtained in the epoxidation of linear cinnamylidenecyclooctanones,\(^{[8]}\) where the \(\gamma,\delta\)-monooxepides isolated in the case of compounds bearing a 2′-hydroxyl group involved intramolecular hydrogen bonding with the carbonyl group, reducing the reactivity of the \(\alpha,\beta\)-double bond and enhancing the reactivity of the \(\gamma,\delta\)-double bond towards the electrophilic DMDO. In the present case, the electron-withdrawing effects of the nitro and carbonyl groups are slightly compensated for by the \(\alpha\)-alkyl chain effect, making the \(C_\alpha=C_\delta\) double bond more reactive towards the electrophilic DMDO. This effect results in the formation of the \(\alpha,\beta\)-monooxepides 5a–c from the oxidation of ortho-nitro-2-cinnamylidenecyclooctanones 3c,f,i, as in the case of the epoxidation of 4-nitrocinnamylidenecyclooctanone with iodosylbenzene and a catalytic amount of salen Mn\(^{III}\).\(^{[9]}\)

### NMR Spectroscopy

The main features of the \(^1\)H NMR spectra of 2-cinnamylidenecyclooctanones 3a–i are the resonances of their vinylic protons. H-3′ appears as a doublet, as a result of the coupling with H-2′ at \(\delta_{\text{H}}\) 7.0–7.2 ppm and the coupling constant \(^{3}J_{\text{H}1′-\text{H}2′}\) 15–16 Hz indicates the \(\text{trans}\) configuration of the \(C_2′=C_3′\) double bond. However, the complete stereochemistry of the \(\alpha,\beta,\gamma,\delta\)-unsaturated carbonyl system was established with the aid of the nuclear Overhauser effect (NOE) cross peaks observed in the corresponding nuclear Overhauser effect correlation spectra (NOESY) (Fig. 1a), which support the close proximity of H-2′ and the aliphatic protons of the cyclonane ring and also of H-1′ and H-3′ and are only consistent with the structure presented in Schemes 1 and 2. The deshielding mesomeric effect of the carbonyl group is responsible for the high resonance frequency of H-1′ and H-3′ \((\delta_{\text{H}}\) 7.4–7.6 ppm) relative to that obtained for H-2′.

The comparison of the \(^1\)H NMR spectra of compounds 3c,f,i with those of 5a–c allowed the detection of a signal, as a doublet \((J\sim7\text{ Hz})\), at \(\delta_{\text{H}}\) 3.92–4.12 ppm and the presence of only two vinylic protons at \(\delta_{\text{H}}\) 6.07–6.18 (doublet, \(J\sim7\) and 16 Hz) and 7.32–7.39 (doublet, \(J\sim16\) Hz). These data are
only compatible with the formation of α,β-epoxides 5a–c, which was also confirmed by the connectivities found in their heteronuclear multiple bond correlation (HMBC) spectra, namely the connectivities of H-3′ with those of the carbonyl carbons (δC 183.1–201.1 ppm) and also of H-1′ and H-2′ with those of C-1′ (δC 131.7–131.9 ppm) (Fig. 1b). In the NOESY spectra of α,β-epoxides 5a–c, there are NOE crosspeaks between the signals H-1′ and H-2′ with those of H-3′ and of the cyclanone rings. These data and the absence of NOE crosspeaks between the signal of H-3′ and the signals of the remaining aliphatic protons confirm the stereochemistry of the oxirane ring depicted in Scheme 2 and Fig. 1b, as expected for an epoxide obtained from a trans-alkene with a concerted mechanism.

The 13C NMR spectra of the α,β-epoxides 5a–c present the signals of the epoxide carbon resonances at δC 61.6–66.6 ppm and those of the vinylic system at δC 127.1–128.2 (C-1′) and 131.8–132.2 (C-2′) ppm.

The 1H NMR spectra of α,β,γ,δ-diepoxides 4a–i are quite complex, presenting two distinct regions (aliphatic and aromatic regions). In the aliphatic region, the presence of two groups of signals indicates that we have a diastereomeric mixture of compounds, and the assignment of the signals of both diastereomers for 4a–i was based on the correlations found in the correlation spectra (COSY) of these compounds. The NOE effects found in the NOESY spectra of these compounds led us to establish the stereochemistry of both diastereomers A and diastereomers B, and the proportion of the mixture as (38%–50%) A, (50%–62%) B, (40%–70%) A, (30%–60%) B and (71%–97%) A (3%–29%) B for compounds bearing five-, six- and seven-membered cyclanone rings, respectively, was calculated from the area of proton signals. This stereochemistry was based on the close proximities between H-3′ and H-3′ and of H-2′ with H-6′′ and some of the aliphatic signals of the cyclanone ring for diastereomers B and between H-3′ and H-2′′ for diastereomers A (Fig. 1a). In the HMBC spectra of α,β,γ,δ-diepoxides 4a–i, the correlations between the carbonyl carbon resonances (δC 192.4–200.9) and the signals of an epoxide ring appearing as a doublet at δH 3.24–3.70 allowed assignment of these proton resonances to H-1′. From the 2D-COSY experiments, all the proton resonances of the α,β,γ,δ-diepoxide system were assigned, H-3′ (doublet at δH 3.24–3.70), H-2′ (doublet at δH 2.97–3.18), and H-3′ (doublet at δH 3.90–4.69). The coupling constant values JH2′–H3′ ~1.7–2 Hz are consistent with a trans configuration of the γ,δ-epoxide, whereas those of JH3′–H2′ are dependent on the size of the cyclanone ring and on the stereochemistry of the diastereomers 4a–i, J 3.8–4.9 Hz for A and J 5.6–6.0 Hz for B, 4d–f, J 4.4–6.0 Hz for A and J 6.1–6.6 Hz for B. 4g–i, J 5.0–6.3 Hz for A and J 6.8–7.2 Hz for B. The aromatic region of the 1H NMR spectra of α,β,γ,δ-diepoxides 4a–i presents several multiplets, which were assigned with the aid of all 2D NMR spectra.

The 13C NMR spectra of the diastereomeric mixture of α,β,γ,δ-diepoxides 4a–i present a duplication of signals with four distinct zones: those at lower-frequency values (δC 22.7–32.2) assigned to the carbon resonances of the aliphatic protons of the cyclanone rings; those at δC 51.6–63.7 belonged to the carbon resonances of the epoxide rings; those at δC 110.1–158.1 due to the carbon resonances of aromatic rings, and those at higher values of frequency (δC 192.4–200.9) attributed to the resonance of the carbonyl carbons. The carbon resonances of the C-3′, C-2′, C-3′, and C-2 of both diastereomers were assigned with the aid of the heteronuclear single-quantum correlation (HSQC) spectra, appearing at δC 51.6–58.1, 57.9–59.7, 59.6–62.2, and 62.0–63.7, respectively. The assignment of the carbon resonances of all compounds was confirmed by the connectivities found in the HMBC spectra (Fig. 1b).

**Conclusions**

Epoxidation of (E,E)-2-cinnamylidene-1-indanones, (E,E)-2-cinnamylidene-1-tetralones, and (E,E)-2-cinnamylidene-1-benzosuberones has been achieved. Dimethyldioxirane in acetone proved to be a convenient oxidant for this purpose, and under these reaction conditions, the major products were a diastereomeric mixture of α,β,γ,δ-diepoxides in each case. The oxidation reaction was more efficient on compounds bearing neutral or electron-rich substituents on the cinnamylidene aromatic ring. The presence of an ortho-nitro substituent slowed down the reaction rate and as a consequence the α,β-monoepoxides were also isolated.
Experimental

Melting points were determined on a Koehler hot-stage apparatus and are uncorrected. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance 300 spectrometer (at 300.13 and 75.47 MHz, respectively); chemical shifts are reported in ppm (δ) using TMS as an internal reference and coupling constants (J) are given in Hz. The ¹H assignments were made using two-dimensional gradient selected correlation spectroscopy (gCOSY) and NOESY (800 ms mixing time) experiments, whereas in the case of ¹³C assignments, we used two-dimensional gradient selected heteronuclear single quantum coherence (gHSQC) and two-dimensional gradient selected heteronuclear multiple bond coherence (gHMBC) (delays for one-bond and long-range J/C couplings were optimized for 145 and 7 Hz, respectively) experiments. The IR spectra were obtained with a Perkin-Elmer 16 PC instrument. Mass spectra were recorded on a VG trio-2 apparatus. Elemental analyses (C, H) were measured in-house with a PC instrument. Mass spectra were recorded on a VG trio-2 apparatus.

General Method for the Preparation of Exocyclic α,β,γ-Unsaturated Ketones 3a–i

A mixture of the cyclic ketone (1a–e, 10.0 mmol), the appropriate trans-cinnamaldehyde (2a–e, 12.0 mmol), 10% aqueous H₂SO₄ (2.38 g, 86%), mp 160–161°C, [α]D (CDCl₃) 3.85 (2H, br s, H-3), 3.91 (3H, s, 2-OCH₃), 6.92 (1H, d, J=8.1, H-3), 6.98 (1H, dd, J=7.7 and 7.5, H-5), 7.10 (1H, dd, J=15.5 and 11.9, H-2′′′), 7.31 (1H, ddd, J=8.1, 7.7, and 1.6, H-6), 7.41 (1H, dd, J=7.6 and 7.4, H-6), 7.42 (1H, d, J=15.5, H-3′′′), 7.47 (1H, dt, J=11.9 and 2.0, H-1′′′), 7.53 (1H, d, J=7.4, H-6′′′), 7.59 (1H, d, J=7.5, H-6′′′), 7.60 (1H, dd, J=7.6, 7.4, and 1.7, H-4′′′), 7.35 (1H, dt, J=7.3 and 1.0, H-8′′′), 7.43 (1H, d, J=15.5, H-3′′′), 7.45 (1H, dd, J=7.4, 7.3, and 1.5, H-7′′′), 7.53 (1H, d, J=11.6, H-6′′′), 7.58 (1H, d, J=7.7 and 1.7, H-6′′′), 7.74 (1H, dd, J=7.3 and 1.5, H-9′′′), δc (CDCl₃) 137.8 (C-1′′′), 137.0 (C-2′′′), 137.0 (C-2′′′), 137.0 (C-2′′′), 137.8 (C-1′′′), 139.2 (C-9a), 139.5 (C-5a), 157.3 (C-2′′′), 198.0 (C-1′′′), m/z 304 (M⁺, 100), 273 (11), 197 (19), 115 (31). νmax/cm⁻¹ 1649, 1604, 1583, 1483, 1452, 1301, 1246, 1162, 1101, 1024, 969, 746, 712. (Found: C 82.77, H 6.69. C₂₁H₂₂O₂ requires C 82.86, H 6.62%).

(E,E)-2-[3-(2-Methoxyphenyl)allylidene]-1-benzosuberone 3h

(2.25 g, 74%), mp 108–109°C. [α]D (CDCl₃) 1.98 (2H, quint, J=8.1, 7.7, 7.5, 7.4, and 1.5, H-9′′′). δc (CDCl₃) 24.5 (C-3′′′), 26.4 (C-4′′′), 31.2 (C-5′′′), 55.2 (2′′′-OCH₃), 111.0 (C-3′′′), 120.7 (C-5′′′), 120.4 (C-2′′′), 125.6 (C-1′′′), 126.9 (C-8′′′), 127.2 (C-6′′′), 128.8 (C-6′′′), 128.9 (C-1′′′), 130.0 (C-9′′′), 131.2 (C-7′′′), 136.3 (C-3′′′), 137.0 (C-2′′′), 137.8 (C-1′′′), 139.2 (C-9a), 139.5 (C-5a), 157.3 (C-2′′′), 198.0 (C-1′′′), m/z 304 (M⁺, 100), 273 (11), 197 (19), 115 (31). νmax/cm⁻¹ 1649, 1604, 1583, 1483, 1452, 1301, 1246, 1162, 1101, 1024, 969, 746, 712. (Found: C 82.77, H 6.69. C₂₁H₂₂O₂ requires C 82.86, H 6.62%).
After the complete consumption of the starting material, the sol-
4d
using 5 equivalents of dimethyldioxirane within 120 h, whereas
α
201 mg, 12%) and that with the lower Rf value identified as the
complete conversion of compounds
4a,b,d,e,g,h into the corre-
responding α,β,γ,δ-diepoxides 4a,b,d,e,g,h was performed by using 5 equivalents of dimethyldioxirane within 120 h, whereas the nitrosotoccluded compounds 3c,f,i could be isolated from tetrahydrofuran (THF) with 18 equivalents of DMDO in 432 h. After the complete consumption of the starting material, the solvent was evacuated under reduced pressure and the residue was crystallized from methanol to afford the diastereomeric mixture of α,β,γ,δ-diepoxides 4a,b,d,e,g,h. Can be interchanged.

Diastereomeric Mixture (50A:50B) of Spiro[indan-1-one-2,2′-[(2-nitrophenyl)-1,2-epoxypropyl]oxirane] 4c

Diastereomeric Mixture (47A:53B) of Spiro[indan-1-one-2,2′-[(2-methoxyphenyl)-1,2-epoxypropyl]oxirane] 4b

Diastereomeric Mixture (36A:62B) of Spiro[indan-1-one-2,2′-[(2-phenyl-1,2-epoxypropyl]oxirane] 4a

Diastereomeric Mixture (29A:71B) of Spiro[indan-1-one-2,2′-[(2-phenyl-1,2-epoxypropyl]oxirane] 4d

Diastereomeric Mixture (29A:71B) of Spiro[indan-1-one-2,2′-[(2-nitrophenyl)-1,2-epoxypropyl]oxirane] 4b

Diastereomeric Mixture (29A:71B) of Spiro[indan-1-one-2,2′-[(2-phenyl-1,2-epoxypropyl]oxirane] 4d

Diastereomeric Mixture (29A:71B) of Spiro[indan-1-one-2,2′-[(2-methoxyphenyl)-1,2-epoxypropyl]oxirane] 4b
Diastereometric Mixture (57A:43B) of Spiro[3,4-dihydro-2H-naphthalen-1-one]-2,2′-[2-(2-methoxyphenyl)-1,2-epoxypropyl]oxirane] 4e

Diastereometric Mixture (70A:30B) of Spiro[3,4-dihydro-2H-naphthalen-1-one]-2,2′-[2-(2-nitrophenyl)-1,2-epoxypropyl]oxirane] 4f

Diastereometric Mixture (7A:29B) of Spiro[6,7,8,9-tetrahydrobenzocyclohepten-5-one]-2,2′-[2-(phenyl-1,2-epoxypropyl)oxirane] 4g

Diastereometric Mixture (7A:29B) of Spiro[6,7,8,9-tetrahydrobenzocyclohepten-5-one]-2,2′-[2-(phenyl-1,2-epoxypropyl)oxirane] 4g

Diastereometric Mixture (7A:29B) of Spiro[6,7,8,9-tetrahydrobenzocyclohepten-5-one]-2,2′-[2-(phenyl-1,2-epoxypropyl)oxirane] 4g

Diastereometric Mixture (7A:29B) of Spiro[6,7,8,9-tetrahydrobenzocyclohepten-5-one]-2,2′-[2-(phenyl-1,2-epoxypropyl)oxirane] 4g

Diastereometric Mixture (7A:29B) of Spiro[6,7,8,9-tetrahydrobenzocyclohepten-5-one]-2,2′-[2-(phenyl-1,2-epoxypropyl)oxirane] 4g
Diastereomeric Mixture (80A:20B) of Spirol[6,7,8,9-tetrahydrobenzocyclohepten-5-one]-2,2′-[2-(2-methoxyphenyl)-1,2-epoxypropyl]-oxirane [4h]

**Diastereomer A:** rel-(2R,3'S,2''S,3''R)-Spirol[6,7,8,9-tetrahydrobenzocyclohepten-5-one]-2,2′-[2-(2-methoxyphenyl)-1,2-epoxypropyl]-oxirane δ₁(CDC13) 1.85–2.00 (2H, m, H-4), 1.95–2.04 (1H, m, H-3), 2.24–2.34 (1H, m, H-3), 2.99 (1H, dd, J 6.0 and 2.1, H-2′′), 2.95–2.98 (1H, m, H-5), 3.08 (1H, dd, J 12.2 and 5.8, H-5), 3.32 (IH, d, J 6.0, H-3′′), 3.90 (3H, d, 2-OCH₃), 4.29 (1H, d, J 2.1, H-3′′), 6.92 (1H, d, J 8.1, H-5′′), 6.99 (1H, d, J 7.4, H-5′′), 7.21 (1H, dd, J 7.4 and 1.7, H-6′′), 7.25 (1H, d, J 7.5, H-6′′), 7.31 (1H, ddd, J 8.1, 7.4, and 1.7, H-4′′′), 7.37 (dt, J 13.7 and 4.4, H-3), 7.43–7.46 (1H, m, H-3), 7.53 (1H, dt, J 13.7 and 4.4, H-3), 2.60 (1H, ddd, J 13.7, 9.4, and 7.3, H-3), 2.98–3.02 (2H, m, H-4), 3.92 (1H, dd, J 7.8 and 0.5, H-3), 7.75 (1H, d, J 15.9, H-2′′), 7.43–7.51 (2H, m, H-4′′′ and H-6′′), 7.52 (1H, dd, J 7.4, H-4), 7.62–7.63 (2H, m, H-5′′′ and H-6′′), 7.68 (1H, dd, J 7.4 and 1.2, H-5), 7.85 (1H, d, J 7.8, H-7), 8.01 (1H, dd, J 8.1, H-3′′′), δC(CDC13) 22.9 (C-2′′′), 25.0 (C-3′′′), 32.2 (C-5′′′), 51.5 (C-3′′′), 55.29 (2′′′-OCH₃), 58.9 (C-2′′′), 62.2 (C-3′′′), 63.0 (C-2′′′), 110.0 (C-12′′′), 124.3 (C-1′′′′′), 124.9 (C-6′′′′), 127.2 (C-9′′′′), 129.1 (C-9′′′′′), 129.5 (C-6′′′′′), 133.5 (C-7′′′′), 136.7 (C-9a′′′), 140.1 (C-5′′′′), 157.8 (C-2′′′′′), 200.9 (C-1′′′′′).

**Diastereomer B:** rel-(2R,3'S,2''R,3''S)-Spirol[6,7,8,9-tetrahydrobenzocyclohepten-5-one]-2,2′-[2-(2-nitrophenyl)-1,2-epoxypropyl]-oxirane [5a]

δ₁(CDC13) 3.34 and 3.44 (2H, AB, J 18.2, H-3), 4.12 (1H, dd, J 6.9 and 0.5, H-3′′′), 6.07 (1H, dd, J 15.9 and 6.9, H-1′′′), 7.35 (1H, d, J 15.9, H-2′′′), 7.43–7.51 (2H, m, H-4′′′ and H-6′′), 7.52 (1H, dd, J 7.4, H-4), 7.62–7.63 (2H, m, H-5′′′ and H-6′′), 7.68 (1H, dd, J 7.4 and 1.2, H-5), 7.85 (1H, d, J 7.8, H-7), 8.01 (1H, dd, J 8.1, H-3′′′), δC(CDC13) 29.0 (C-3′′′), 61.6 (C-3′′′), 66.6 (C-2′′′), 124.1 (C-7′′′), 124.8 (C-3′′′′′), 126.7 (C-4′′′′), 128.1 (C-6′′′′), 128.2 (C-1′′′′′), 128.9 (C-4′′′′′), 131.7 (C-1′′′′′), 131.8 (C-1′′′′), 135.4 (C-5′′′′), 135.7 (C-7a′′′′), 135.8 (C-8′′′′), 147.5 (C-2′′′′′), 150.9 (C-3a′′′′), 199.5 (C-1′′′′). m/z (Electrospray ionization (ESI)-MS): 308.0919. C₁₅H₁₃N₂O₃ requires [M + H]⁺ 308.0923.

Diastereomeric Mixture (97A:3B) of Spirol[6,7,8,9-tetrahydrobenzocyclohepten-5-one]-2,2′-[2-(2-nitrophenyl)-1,2-epoxypropyl]-oxirane [4i]

**Diastereomer A:** rel-(2R,3'S,2''S,3''R)-Spirol[6,7,8,9-tetrahydrobenzocyclohepten-5-one]-2,2′-[2-(2-nitrophenyl)-1,2-epoxypropyl]-oxirane δ₁(CDC13) 1.84–1.93 (2H, m, H-4), 2.00 (1H, dd, J 14.6, 6.7, and 3.3, H-3′′′), 2.25 (1H, dd, J 14.6, 9.5, and 7.8, H-3′′′), 3.00 (1H, dd, J 6.3 and 2.1, H-2′′′), 2.96–3.02 (1H, m, H-5′′′), 3.14 (1H, d, J 14.1, 10.1, H-2′′′), 3.46 (1H, d, J 6.3, H-3′′′), 4.60 (1H, d, J 2.1, H-3′′′), 7.23 (1H, d, J 7.6, H-6′′), 7.36 (1H, dt, J 7.6 and 1.2, H-7), 7.52 (1H, d, J 7.6, H-5′′′), 7.37 (1H, d, J 7.6 and 0.9, H-8), 7.39 (1H, d, J 15.5, H-2′′′), 7.45–7.51 (1H, m, H-4′′′ and H-6′′), 7.51 (1H, d, J 7.6 and 1.4, H-7), 7.60–7.64 (2H, m, H-5′′′′ and H-6′′′′), 7.79 (1H, dd, J 7.6 and 1.4, H-9), 8.02 (1H, d, J 7.8, H-3′′′′′), δC(CDC13) 22.7 (C-4′′′′), 24.5 (C-3′′′′), 32.1 (C-5′′′′), 62.8 (C-3′′′′′), 65.7 (C-2′′′′′), 124.8 (C-3′′′′′).
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References


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